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THE

PHYSICAL REVIEW.

THE DISCHARGE OF ELECTRICITY FROM POINTED CONDUCTORS.

By John Zeleny.

1. In a previous paper [1] are given the results of some experiments on the discharge of electricity from a set of points which consisted of cylindrical wires of different diameters whose ends were either hemispherical or plane. The points were placed opposite a brass disc and were enclosed in a cylindrical vessel containing dry air.

It was found that the discharge from points of this character gives consistent results which can be readily reproduced, and the way that the discharge depends upon the diameter of the point was given special consideration.

The apparatus, which is fully described in the paper mentioned, has been used for studying the discharge from steel needle points of various degrees of sharpness and from brass conical points of various sizes, and the results are here recorded together with those of some other experiments on point discharge.

The subject-matter is considered under the following subdivisions :

(*a*) Positive discharge from steel needle points..... §§ 2, 3
(*b*) Relation between current, voltage, minimum potential, and diameter of points..... § 4
(*c*) Negative discharge from steel needle points..... § 5
(*d*) Formation of oxides on steel points..... § 6
(*e*) Positive discharge from 12° conical points..... §§ 7, 8
(*f*) Negative discharge from 12° conical points..... § 9
(*g*) Discharge to different parts of a spherical surface..... §§ 10, 11
(*h*) Discharge at different pressures..... §§ 12, 13
(*i*) General remarks..... § 14
(*j*) Summary..... § 15

[1] J. Zeleny, Phys. Rev., 25, p. 305, 1907.

POSITIVE DISCHARGE FROM STEEL NEEDLE POINTS.

2. The steel needle points used were prepared from ordinary sewing needles, a variety of sizes of the points being obtained by altering the ends of some of the needles on an oil stone.

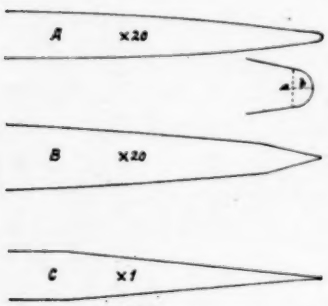


Fig. 1.

Two kinds of commercial needles were met with. In the one (see *A*, Fig. 1) the angle between the opposite walls of the needle increases gradually as the point is approached, reaching a value of from 10° to 12° at the point itself. In the other kind (see *B*, Fig. 1) there is a sudden increase in the taper near the end of the needle, the angle changing at a distance of about one half a millimeter to a millimeter from the end, from about 10° to over 20° and to as much as 30° in one make. The sharpest points are found on needles of this type. Usually the finest needles were found to be of the first type and the coarser ones of the second type but in an assorted package from one maker the needles of all sizes were of the second type.

The sharpness or size of the needle point will be designated in each case by giving the diameter of the cross-section of the needle at a place where this diameter (*a*, Fig. 1) is twice the distance (*b*, Fig. 1) of this cross-section from the tip of the needle. The measurements were made with the stage micrometer of a microscope, the location of the cross-section specified being estimated by eye alone.

In order to describe more exactly the general nature of the needles used, not only is this diameter of the point stated for each needle but its length and maximum diameter are also given, together with the angle of the average taper for the first two or three point-diameters from the end. It has been found that one of the chief differences between different needles as regards point discharge lies in the value of the taper at the end. The angle of this taper usually increases as the points get sharper, because it is both difficult and inadvisable to make very sharp points with this angle small.

Preliminary experiments made in the open air with a promiscuous lot of needles gave results which varied quite regularly with the

diameter of the points, but among the finest points one would be found now and then with the taper exceptionally obtuse, which would give results considerably different from the rest. The largest difference observed was one of seven per cent., in the voltage required to produce a given current.

The experiments here described were carried out in exactly the same way as those described in the paper already referred to. The needles were supported above the plate by means of a brass rod, in the end of which a slot was provided for holding them axially.

3. The results obtained for the positive discharge in dry air with a number of selected needles placed at a distance of 1.5 cm. from the plate, are given in Table I. The temperature was practically 19° C. and the air pressure 74.7 cm. throughout the whole series of experiments.

TABLE I.

Positive Discharge from Steel Needle Points. Distance from Plate = 1.5 *Cm.*

Point Number.	1	2	3	4	5	6
Diameter of Point in Mm.	.0068	.012	.055	.096	.198	.364
Length of Needle in Mm.	34.7	x	39.7	36.3	49.0	45.5
Max. Diameter of Needle in Mm.	.51	x	.82	.57	1.17	1.03
Taper of Point.	26°	x	24°	12°	9°.2	7°.3
Starting Potential.	2,650	2,700	2,900	3,025	3,550	4,375
Potentials in volts with corresponding currents in 10^{-7} amperes.	3,000	3,000	3,500	3,500	4,000	4,500
	2.8	2.3	5.7	4.5	5.9	2.3
	4,000	3,500	4,000	4,000	5,000	5,000
	13.6	6.8	11.9	10.7	19.2	9.6
	5,000	4,000	5,000	5,000	6,000	6,000
	28.3	13.6	26.6	26.0	40.1	28.8
	6,000	5,000	6,000	6,000	7,000	7,000
	50.9	28.8	49.2	47.5	64.4	50.9
	7,000	6,000	7,000	7,000	8,000	8,000
	73.5	50.3	73.5	73.4	92.7[1]	79.1
	8,000	7,000	8,000	8,000	9,000	9,000
	104.5[1]	76.3	101.7	102.3	131.1[1]	117.0
		8,000	8,350	9,000		9,500
		104.5	118.1	141.2		141.3
		8,500				
		125.4				

[1] Current more or less intermittent as indicated by telephone.

The results have been reduced to a pressure of 74 cm. and a temperature of 22° C. to make them correspond to the conditions prevailing in the experiments described in the previous paper. The way in which this reduction is made is explained in §§ 20 and 21 of

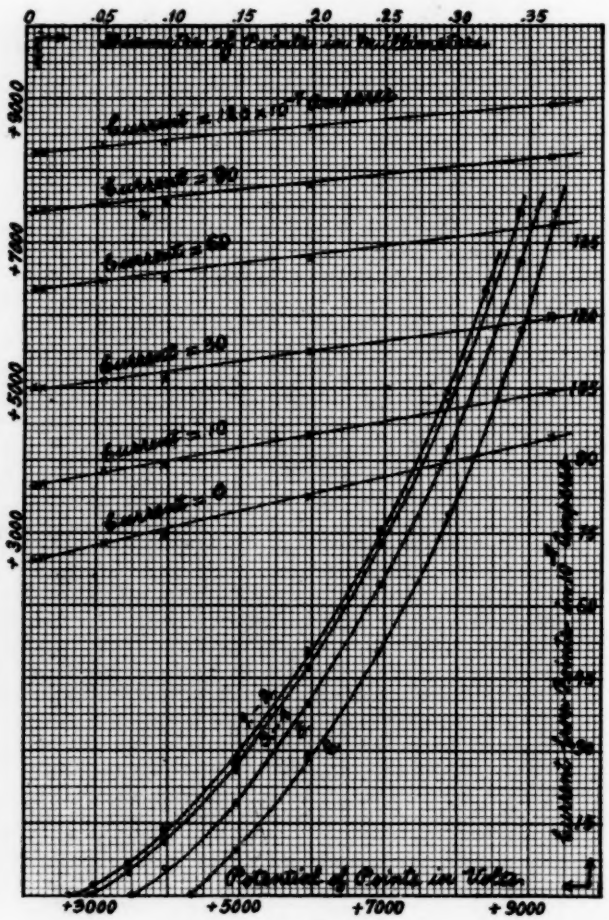


Fig. 2.

the paper mentioned, and in this case amounted to reducing the potentials by about 1.3 to 1.5 per cent. These reduced results are shown graphically in Fig. 2.

The lower right-hand curves give the relation between the voltage and the current for the different points. The values for the

points no. 1 and no. 2, and for the points no. 3 and no. 4 are so close together that but one curve is drawn for each of the two cases.

The curves in the upper part of the figure were drawn to show whether there is any relation between the size of the points and the voltage necessary to produce a given current. The potentials taken from the potential-current curves were plotted against the size of the points for each of the currents given. It is seen that there is good regularity in the results and that in each case the potential increases linearly with the size of the point. In view of this regularity, it is now possible to construct from these curves a potential-current curve for a needle point of any size, provided however that the angle of the taper at its point approximates to that on those needles here used which are of about the same point diameter.

The fact that the voltage required to produce any current increases linearly with the diameter of the point is incidental to the way that the angle of the taper increases as the points diminish in diameter. Had the taper of the finest points been as small as that of the larger ones their potentials for the same current would have been smaller than they are.

Relation Between Current, Voltage, Minimum Potential, and Diameter of Points.

4. The relation between the current and voltage for any one point is fairly well represented by Warburg's formula, $C = aV(V - M)$, where V is the voltage of the point, M the minimum voltage required to start a current, and a a constant whose value depends upon the point used. This constant was found to increase linearly with the diameter of the point, so that it is possible to represent the results for all of the points by one formula, the current in amperes being given by,

$$C = 2.58 \times 10^{-13}(1 + .319d)V(V - M),$$

where d is the diameter of the point in millimeters.

In Table II., a comparison is made of the values of the current obtained for several potentials, by the use of this formula and the observed values as taken from potential-current curves similar to but larger than those in Fig. 2.

TABLE II.

Comparison of Observed Currents with those Calculated by the Formula, $C = 2.58 \times 10^{-13} (1 + .319d)\ V(V - M)$.

Diameter of Point.		.0068	.012	.055	.096	.198	.364
M		2,615	2,665	2,860	2,985	3,505	4,320
Voltage.							
3,000	Current calc.	3.0	2.8				
	observ.	3.0	2.6				
4,000	Current calc.	14.3	13.8	12.0	10.8	5.4	
	observ.	14.3	14.0	12.1	11.3	5.7	
5,000	Current calc.	30.9	30.2	28.0	26.7	20.5	9.8
	observ.	30.2	30.2	28.0	27.3	20.2	10.3
6,000	Current calc.	52.6	51.9	49.4	48.0	41.1	27.3
	observ.	52.0	52.0	49.7	48.6	40.6	29.0
7,000	Current calc.	79.4	78.7	75.9	74.6	67.2	54.0
	observ.	79.3	79.3	76.6	75.3	66.7	53.2
8,000	Current calc.	111.6	110.9	107.8	106.6	98.6	84.8
	observ.	112.3	112.3	108.2	107.6	100.0	83.2
9,000	Current calc.			144.7	144.0	135.8	121.3
	observ.			143.4	143.4	136.5	122.4

It is seen that the two sets of values are in good agreement.

Since the minimum potential required to start a current increases linearly with the diameter of the point, as is shown by the potential-diameter curve for $C = 0$ in Fig. 2, its value in volts can be represented by the relation, $M = 2{,}590 + 4{,}750d$, where d is again the diameter of the point in millimeters.

NEGATIVE DISCHARGE FROM STEEL NEEDLE POINTS.

5. The results which were obtained for the negative discharge in dry air from the same set of needle points as used above, are given in Table III. The distance of the points from the plane was again 1.5 cm. The temperature throughout the readings was nearly constant at 19° C. and the air pressure was 74.7 cm. The starting potential was determined first in each case and then the currents were obtained for gradually increasing voltages. Where readings were repeated the average value is given.

The results, reduced to a pressure of 74 cm. and a temperature of 22° C., are represented graphically by the lower right hand curves in Fig. 3. The points agree quite well with their respective

curves. Nevertheless, the smaller negative currents often show considerable irregularity. This is especially the case after a point has been used with the higher currents, as some resistance to the flow of small currents seems to be introduced

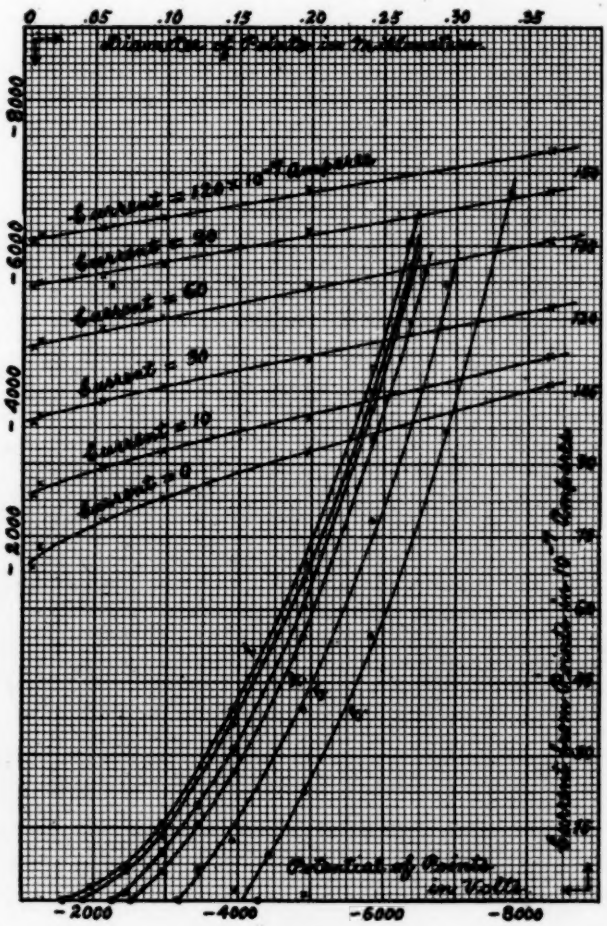


Fig. 3.

thereby on the surface of the point, so that the values now obtained with a given voltage are much below the normal values obtained at first. The two points marked by crosses below the curves for the two largest points in Fig. 3, represent experimental results and show how large this deviation may be and to what sized

TABLE III.

Negative Discharge from Steel Needle Points. Distance from Plate = 1.5 Cm.

Point Number.			1	2	3	4	5	6
Diameter of Point in Mm.			.0068	.012	.055	.096	.198	.364
Starting Potential.			1,600	1,900	2,250	2,550	3,225	4,350
Potential of points.	2,000	Current from points in 10^{-7} amperes.	2.8					
	2,500			7.3	3.0			
	3,000		16.0	14.3	10.1	5.9		
	3,500				19.6	15.7	6.2	
	4,000		39.2	36.4	31.4	26.9	12.3[1]	
	4,500							9.5[1]
	5,000		69.4	66.1	60.5	54.3	39.2[1]	22.4
	6,000		109.8	104.7	101.4	95.2	78.4	54.9[1]
	6,500		135.5	130.6	127.7	119.3		
	6,700					129.9		
	7,000						127.2	96.9
	7,925							145.6

currents it may apply. As the voltage is increased when these abnormal conditions obtain, the resistance mentioned disappears more or less suddenly and the current rises to its normal value.

The curves in the upper part of Fig. 3 show the relation between the size of the points and the voltage required to produce the current given in each case. These curves can be used as before for the construction of a potential-current curve for a point of any intermediate diameter, when this has a taper corresponding to that of the points here used. The results for one of the points nos. 1 and 2 do not agree well with the rest, and there is reason to believe that the discharge from no. 2 was retarded for some reason.

The relation between the current, voltage and the diameter of the points is not as regular in this case as it was for the positive discharge but is given approximately by the formula,

$$C = 4.18 \times 10^{-13}(1 + .63d)V(V - M),$$

where the letters have the same significance as before.

FORMATION OF OXIDES ON STEEL POINTS.

6. After a discharge has passed for some time from a steel point in air, it is found that some substance has accumulated at the end

[1] Currents marked by a figure ([1]) were somewhat intermittent.

of the point. This is especially true if the point has been discharging positive electricity. The difference between the positive and the negative discharges in this respect is very marked.

As an example of this action *A*, in Fig. 4, shows the appearance under the microscope, of the end of a steel needle point after a positive current of about 10^{-5} amperes had been flowing from it for five minutes. The substance on the end of the point is of a reddish brown color, and is doubtless an oxide of iron since it does not form on a platinum point. *B*, Fig. 4, shows the same point after the same current had been flowing from it for 44 minutes. It is noticed that the material is attached to the point in irregular pieces which extend outward some little distance. The substance is readily removed with a cloth leaving the surface of the point apparently as bright as ever. It is natural that the presence of this material should have some effect upon the discharge current, and points which have been used for some time must be cleaned to have them regain their normal condition.

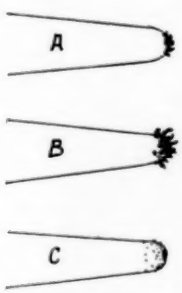


Fig. 4.

When the same point was used with a negative current of the same value for five minutes, it showed no change in appearance. Gradually, however, a readily removable tarnish appeared on the point for a distance of a little over its diameter, dulling somewhat the bright luster of that portion of the needle. The appearance seemed to indicate an accumulation of a lot of fine dark particles. After the negative current had been flowing for over an hour, the point had the appearance shown by *C* in Fig. 4. The little patch at the very end of the point was of the same reddish-brown color as the accumulation in the case of the positive discharge, but it was in the form of a thin coating. The rest of the deposit was black and some of the larger particles showed a black luster as if they were coal dust.

The reason why the oxide forms so much more readily during the positive discharge than it does during the negative, may be that in this case negative ions of oxygen are carried from the surrounding air to the metal surface, and forming as they do the negative parts

of the iron oxide molecules they unite more readily with the iron than do the positive ions which are carried to the metal surface during the negative discharge.

The deposit can hardly be due to the ozone which is formed by the discharge, attacking the iron, as the ozone is formed in not very unequal quantities during both the positive and negative discharges.

POSITIVE DISCHARGE FROM 12° CONICAL POINTS.

7. Since the taper at the ends of steel needles varies so much for the different needles and of necessity changes along the length of the needle, it was thought worth while to study the discharge from a number of points where this angle is the same for all and remains unchanged for some distance back from the point. Six brass conical points were therefore made, the angle of whose cones was 12° for all alike. These cones were 6.35 mm. in diameter at the base (see *C*, Fig. 1), and tapered uniformly to the points which were rounded off so as to be of different diameters. The diameters were measured in the same way as was done with the steel needles.

TABLE IV.

Positive Discharge from 12° *Conical Points.*

Point Number.			1	2	3	4	5	6
Diameter of Point in Mm.			.060	.107	.336	.464	.64	1.09
Starting Potential.			2,825	3,125	4,500	5,000	5,850	7,525
Potential of points in volts.	3,000	Current from points in 10^{-7} amperes.	1.7					
	3,500		6.2	3.9				
	4,000		12.3	9.0				
	4,500		19.2	15.1				
	5,000		27.4	23.5	6.2			
	5,500		38.1	33.4	14.6	7.8		
	6,000		48.1	43.1	22.9	15.7	3.3	
	6,500		59.9	54.8	32.8	25.2	11.8	
	7,000		72.2	66.6	43.7	35.3	21.3	
	7,500		83.9	78.4	54.8	45.4	30.2	
	8,000		98.5	94.0	67.7	59.3	42.5	10.6
	8,500		117.7	112.5[1]	85.0	75.0	58.1	24.1
	9,000		136.6[1]	132.0[1]	103.0	92.9	75.0	39.2
	9,500				124.1[1]	114.0[1]	95.1	57.1
	9,725				132.5[1]			
	9,825					128.8[1]		
	10,000						115.2	76.1

[1] Currents marked with a figure ([1]) were somewhat intermittent.

The results obtained for the positive discharge in dry air from these points when placed at a distance of 1.5 cm. from the plate in the same apparatus as used before, are given in Table IV:

The temperature during the experiments was practically constant

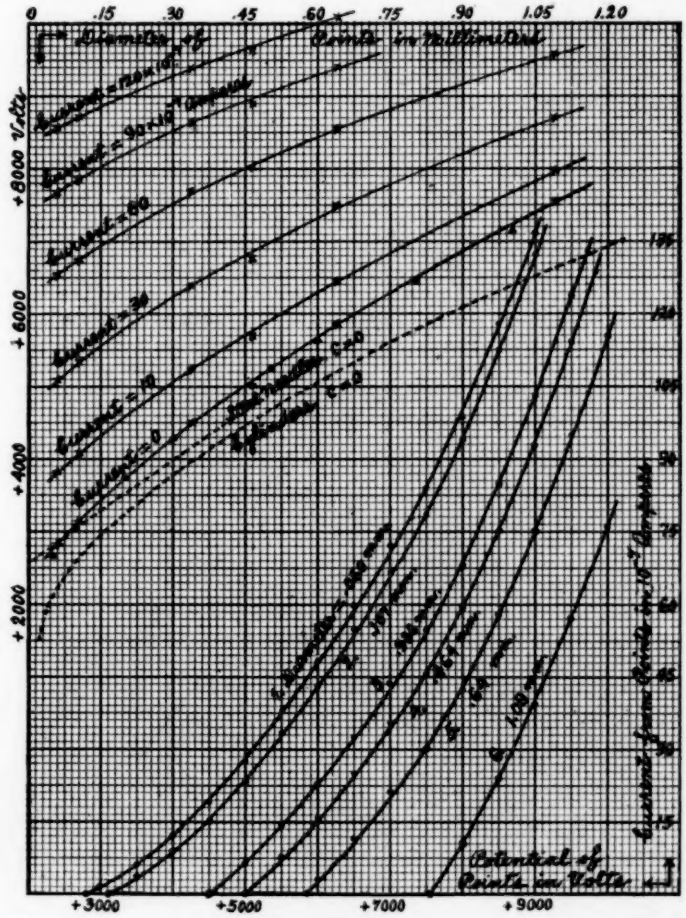


Fig. 5.

at 21° C., and the pressure was 73.7 cm. To reduce the results to a temperature of 22° C. and a pressure of 74 cm. as has been done in the other cases would only require a correction of the order of one tenth of one per cent.

The results are represented graphically by the curves in the lower right hand portion of Fig. 5.

The individual readings are seen to be in good agreement with their respective curves. In the upper part of the figure are shown the potential-diameter curves for the various currents given, the points for each current being taken from the potential-current curves in the lower part of the figure. The good agreement of these points with their respective curves shows the regularity in the results, the values from any point being dependent upon the size of the point only, and not upon any peculiarities of its surface.

8. The relation between the current and potential may be represented again fairly well for each point by the formula, $C=aV(V-M)$, although at the highest voltages used the observed values tend to be larger than what this formula demands. The values of a obtained for the smallest points are nearly alike, but they increase rapidly for the larger points, so that the current in amperes from any point may be approximately represented by the formula,

$$C = 2.49 \times 10^{-13}(1 + .176d^3)V(V - M),$$

where d is the diameter of the point in millimeters. In the cases previously considered d appeared in the first power.

TABLE V.

Comparison of Observed Currents with those Calculated by the Formula, $C = 2.49 \times 10^{-13}(1 + .176d^3)V(V - M)$.

Diameter of Point in Mm.		.060	.107	.336	.464	.64	1.09
M		2,825	3,125	4,500	5,000	5,850	7,525
Voltage.							
4,000	Current calc.	11.7	8.7				
	observ.	12.2	8.9				
5,000	Current calc.	26.8	23.4	6.3			
	observ.	27.9	23.7	6.2			
6,000	Current calc.	47.4	43.0	22.6	15.2	2.4	
	observ.	48.0	43.0	22.7	15.3	2.8	
7,000	Current calc.	72.6	67.4	43.8	36.0	21.0	
	observ.	71.0	66.0	42.4	34.5	20.0	
8,000	Current calc.	101.5	97.1	70.1	60.8	44.7	11.6
	observ.	100.3	94.1	68.5	59.6	43.0	10.6
9,000	Current calc.	138.2	130.7	101.6	91.2	73.9	40.6
	observ.	136.6	132.0	103.0	93.0	75.0	40.0
10,000	Current calc.					108.1	75.6
	observ.					115.0	76.0

The degree of agreement between the values obtained from this formula and the experimental values taken from the potential-current curves in Fig. 5, is shown for several potentials by the comparison given in Table V.

The potential required to start a current increases with the diameter of the point, in a more complex manner than it did in the cases given before, but its value may be obtained quite accurately for any point by means of the formula,

$$M = 1{,}980 + 5{,}200 d^{\frac{1}{2}},$$

where d is again the diameter of the point in millimeters.

Some values obtained from this formula have been plotted as triangles on the curve for $C = 0$ in Fig. 5, and the good agreement of these points with the observed values is to be noted.

One of the main physical differences between steel needles and these conical points is that at some distance back from the point the needles approximate to cylinders while in the cones, of course, no such change takes place. The difference in the formulæ necessary to represent the results in the two cases is probably due to this difference.

Negative Discharge from 12° Conical Points.

9. The results obtained for the negative discharge in dry air from the same conical points as used above when placed at a distance of 1.5 cm. from the plate, are given in Table VI. The temperature throughout was approximately 18°.2 C. and the pressure 72.2 cm.

The results, for the larger points especially, are quite irregular. With the point .64 mm. in diameter the current fluctuated so much that it was not possible to take any readings at all. A star is placed opposite the values of those currents which are given where the telephone indicated an intermittence. The values for the smallest currents were erratic and fluctuated somewhat. Some irregular resistance to the discharge seemed to be present on the surface of the point which only disappeared after the current had reached a certain value.

The results are shown graphically in the lower part of Fig. 6. In drawing the curves some of the erratic values for the smaller

currents were disregarded altogether. The results are not regular enough, as a whole, to permit of being used to test any formula, but Warburg's formula appears to hold well for the smallest points, the value of the constant for point no. 1 being 4.3, in the same units as have been used throughout.

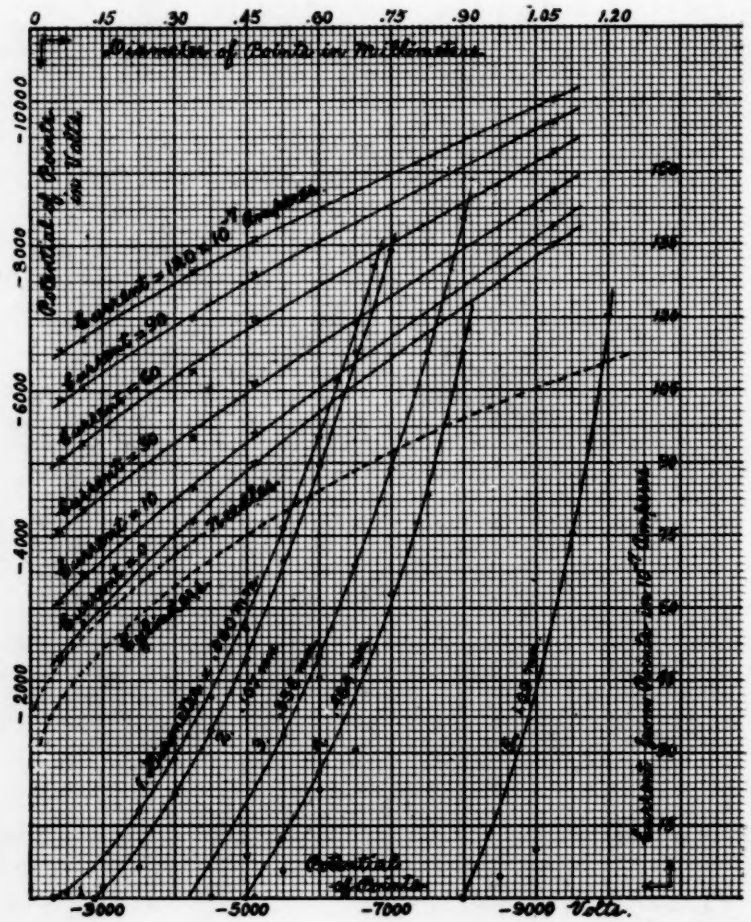


Fig. 6.

The curves in the upper part of Fig. 6 again give the relation between the size of the points and the voltage necessary to produce the currents stated in each case. The agreement of the individual points with these curves seems to justify the drawing of the potential-

current curves without regard to the low erratic values of the current which so often appeared.

Discharge to Different Parts of a Spherical Surface.

Table VI.

Negative Discharge from 12° Conical Points.

Point Number.			1	2	3	4	5
Diameter of Point in Mm.			.060	.107	.336	.464	1.09
Starting Potential.			2,300	2,875	4,500?	5,100	8,000
Potential of points in volts.	2,500	Current from points in 10^{-7} amperes.	1.2				
	3,000		3.9	2.0			
	3,500		18.0	6.2			
	4,000		28.7	21.7			
	4,500		41.4	34.7			
	5,000		55.4	49.5	8.9*		
	5,500		76.5	69.2	33.8	12.5*	
	6,000		95.6	89.5	50.0	26.0*	
	6,500		118.8	113.0	68.7	30.4*	
	6,750		130.5				
	7,000			133.9	89.0	63.0	
	7,500				112.6	83.3*	
	8,000				140.8	112.6	
	8,500						4.5*
	9,000						10.1*
	9,500						75.5*
	10,000						120.5*

10. Warburg[1] has found the law according to which the current flowing from a point to a plane distributes itself over the area of the plane. It seemed of some interest to see how the current would distribute itself to the various parts of a spherical surface from a discharging point situated at its center of curvature, inasmuch as the electrostatic field is much simpler in this case and approximates at least roughly to that between two concentric spheres.

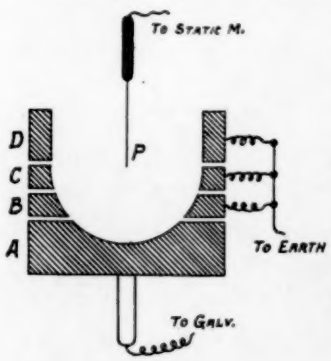


Fig. 7.

The apparatus used is shown in section in Fig. 7.

[1] E. Warburg, Wied. Annal., 67, p. 69, 1899.

A brass cylinder was divided into the four parts A, B, C and D, which were separated by spaces of one millimeter and held in place by means of sealing wax. The cavity in the parts A, B and C formed a hemisphere with a radius of 1.5 cm. The portions of the hemisphere on the three sections were of equal area. The effective areas of these sections for receiving the current, however, include parts of the air spaces between them, and as section B has air spaces on both sides, its effective area is about ten per cent. larger than that of section A. Section D was one centimeter in height and its interior surface was a cylinder three centimeters in diameter, thus forming a continuation of the spherical surface in the other sections.

The point P was a brass cylindrical wire .18 mm. in diameter. It had a rounded end which was placed at the center of the spherical surface in A, B and C. The auxiliary apparatus was the same as that used in the other experiments.

In taking readings each of the sections A, B, C and D was connected in turn to the galvanometer while the rest were joined to earth. The readings were taken with the apparatus in the open air, in the winter when the humidity was low, so that the results are but little different from what would have been obtained had dry air been used.

One set of readings taken for both the positive and the negative discharges is given in Table VII. The temperature was 21° C. and the air pressure was 74.8 cm.

TABLE VII.

Discharge to Different Parts of a Spherical Surface.

Positive Discharge.					Negative Discharge.				
Voltage of Point.	Current in 10^{-7} Amperes Flowing to				Voltage of Point.	Current in 10^{-7} Amperes Flowing to			
	A	*B*	*C*	*D*		*A*	*B*	*C*	*D*
3,500	4.2	4.2	2.2		2,750	1.8	1.6	1.6	—
4,000	7.2	7.7	6.0	.06	3,000	4.4	3.9	3.5	—
5,000	15.4	16.5	14.9	3.3	3,500	—	—	10.2	3.0
6,000	26.4	28.6	26.4	10.7	4,000	15.4	17.1	16.5	8.3
6,500	33.0	—	—	—	5,000	32.1	36.3	34.7	26.4
7,000	39.8	42.9	40.7	20.9	5,500	45.1	50.6	48.4	39.6
Min. voltage	2,800	2,850	3,075	—	Min. voltage	2,550	2,625	2,625	3,075

11. When due allowance is made for the inequality of the effective areas of the different sections as explained above, it is seen that the current is quite uniformly distributed over the whole surface of the hemisphere, for all but its smallest values. The effective area of B is about ten per cent. larger than that of A, and the currents going to it are larger by about the same amount. The effective area of C is also very likely somewhat larger than that of A, but as the upper air space is outside of the hemisphere it is more difficult to estimate its effect.

The values obtained by computing the current per square centimeter from the current flowing to the whole hemisphere, can be represented quite well for the positive discharge by the formula,

$$C = .60 \times 10^{-13} V(V - 2{,}800) \text{ amperes},$$

where V is the voltage of the point and 2,800 is the voltage at which the current started to flow to the central section.

Similarly the negative current in amperes per square centimeter can be represented by

$$C = 1.23 \times 10^{-13} V(V - 2{,}550).$$

The values of the potential required to start a current in this case are nearly 200 volts smaller than is required to start a current from a point of the same size when placed at a distance of 1.5 cm. from a plane.[1]

The positive current flowing to the whole hemisphere at any voltage is not quite twice as large as would flow to a plane at the same distance, while the negative current flowing to the hemisphere is a little more than twice as large as the corresponding current flowing to a plane.[2]

Most of the current which flows to the section D at the higher voltages is due to a discharge from the side of the wire point, since owing to their high velocity it is not likely that many of the ions are forced out from the hemispherical volume by mutual repulsion.

When the section D was removed, the current received by section C was considerably smaller than that flowing to either A or B.

[1] J. Zeleny, loc. cit., see Figs. 2 and 5.
[2] Ibid.

A small hole was bored in the center of a middle section of an apparatus similar to the above, and the pressure in the air was measured at that point during a discharge, by means of a sensitive manometer. The value obtained was about one third of that calculated[1] on the supposition that there are no convection currents. In the middle of the next section the pressure was still smaller.

DISCHARGE AT DIFFERENT PRESSURES.

12. The results of some experiments which were carried out some time ago on the discharge from a point in dry air under pressures varying from that of the atmosphere to the very lowest at which a discharge could be made to pass, will now be described briefly.

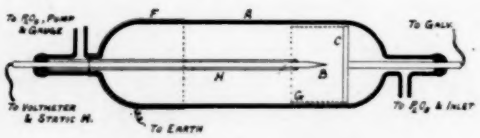


Fig. 8.

The apparatus that was used is shown in Fig. 8, the auxiliary parts being practically the same as were used above.

The glass tube A, 4.6 cm. in diameter, contained the point B and the plate C. The point B consisted of a brass rod, 3.2 mm. in diameter, whose end was turned to a 15° cone, the diameter of whose point was .068 mm.

The rod was covered with the glass tube H, up to a distance of 1.6 cm. from the point. The brass plate C which received the current had a wire-gauze cylinder G attached to its rim. This protected the space between the point and the plate from the effects of any electrification that might collect on the walls of the glass tube. The distance between the point and the plate was one centimeter.

The part F of the glass tube was covered with earthed tinfoil to prevent the spreading over the outer surface of static charges from the high potential wire. A static machine was used for producing potentials above 1,000 volts, and a battery of storage cells was used for potentials below 1,000 volts.

Potential-current curves were obtained for both the positive and

[1] A. P. Chattock, Phil. Mag., 48. p. 401, 1899.

the negative discharges, for a large number of decreasing pressures until the discharge ceased to pass with the potential of the point at over 10,000 volts. The nature of the results obtained is shown by the curves in Fig. 9, which indicate how the potential required to

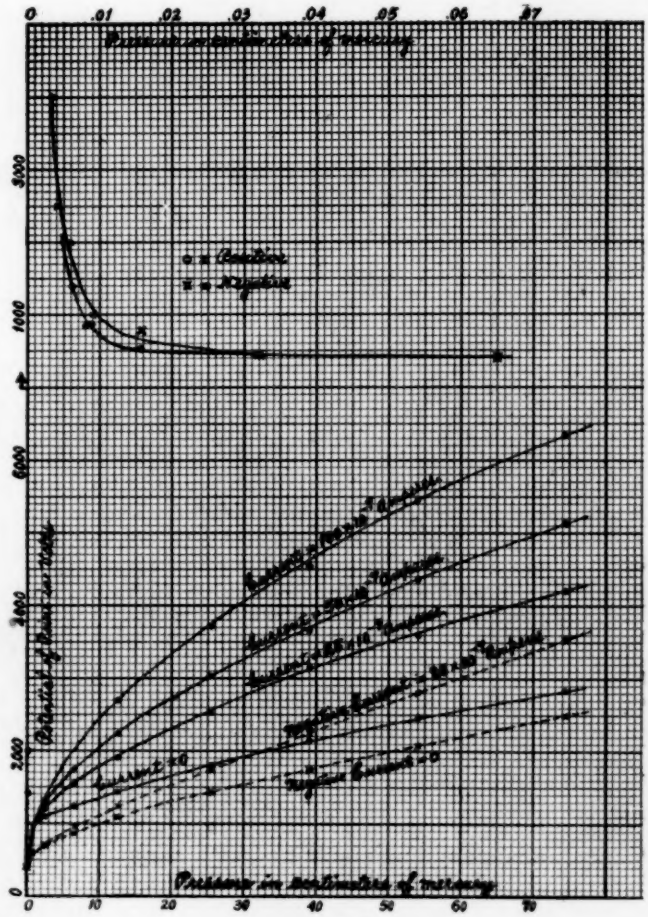


Fig. 9.

produce a given current changes with the pressure of the gas. The curves given were obtained from the potential-current curves for the different pressures, by plotting the potentials required at these pressures to produce the current stated in each case.

The full line curves are for the positive discharge and the two

broken line curves are for the negative discharge. The only values used in plotting the positive potential-current curves were those where the current was steady as indicated by the telephone receiver which was placed in the galvanometer circuit.

In considering the results it must be borne in mind that not only does the nature and the appearance of the discharge change as we reach the lower pressures, but in addition the area of the electrodes to and from which the discharge passes, increases until at the lowest pressures the current passed between the whole exposed surface of the point and the whole surface of the plate and the gauze cylinder attached to it.

At many of the low pressures the current would only begin with a high value, and as the voltage was diminished the current would drop as suddenly to zero.

It is seen from the curves in the figure that at the lowest pressures the current increases rapidly with change of voltage, since the potential-pressure curves for the different currents converge very rapidly for pressures below five centimeters, and below one centimeter the different curves are not distinguishable on the scale used.

For the positive discharge the voltage required to produce a current changes rapidly from about 1,000 volts for a pressure of one centimeter to a minimum of about 400 volts. With the negative discharge, for the same range of pressure, the voltage only changes from about 600 to 400 volts, the minimum voltage being the same as for the positive.

The curves in the upper part of Fig. 9 show how, at the lowest pressures used, the voltage required to produce a current changes with the pressure. It is seen that for a considerable range of pressure the voltage remains about constant and the same for both kinds of discharge, but that as the pressure is diminished below .01 cm. the potentials rise rapidly for both discharges.

With the positive discharge no current could be obtained with over 12,000 volts when the pressure was reduced to .0042 cm., while for the negative discharge, when the pressure was as low as .0023 cm., a little flash of light appeared in the tube now and then with the potential somewhat over 12,000 volts.

It is worthy of notice that the lowest potential at which either the

positive or the negative discharge would take place at any pressure, is about 400 volts, which value approximates to the cathode fall of potential in air which is observed in vacuum tubes where larger sized electrodes are used.

13. The general luminous aspect of the steady positive discharge at the different pressures will now be described.

(*a*) The light was confined to the immediate neighborhood of the point, appearing as a violet tinted speck of light, for all pressures down to 6.5 cm., at which pressure a violet glow extended back over the point for a distance of about two millimeters, the light at the point itself being more intense than that farther back.

(*b*) At a pressure of 2.5 cm. this glow had already spread back over the whole exposed surface of the point (1.6 cm.).

The discharge at this pressure would usually start with an instantaneous flash of light, consisting of a bright speck of light on the point itself, with a brush of light extending nearly to the plate, where a dark space separated it from a luminous coating on the plate itself. After this one flash, the appearance of the discharge changed to the violet glow over the point, described at first. When the static machine was stopped, the current gradually diminished and just as the discharge ceased a flash similar to that at the beginning would pass through the tube.

Sometimes the current continued intermittent, having to the eye the general appearance described for the flash discharge. At other times, again, a combination of the steady and intermittent discharges was noticed. These may not have been simultaneous, the discharge possibly alternating rapidly between the two kinds.

(*c*) At a pressure of .9 cm. the appearance of the steady discharge was the same as at 2.5 cm. pressure. Once at this pressure the current alternated back and forth between the steady and intermittent kinds described under (*b*), being intermittent for 20 seconds and then steady for 45 seconds, for a period of over 20 minutes, when the current was discontinued.

This indicates that during one of the discharges some surface condition necessary for its existence is altered by the discharge, so that the discharge changes to the other kind during which the original surface condition is recovered, enabling the discharge to change back again to the first kind.

(*d*) At a pressure of .39 cm. the glow over the whole point had become somewhat wider than it was in the last case, being now about one millimeter wide and fading off into the gas.

(*e*) At a pressure of .19 cm. the glow over the point was still less sharply defined and extended for about three millimeters into the gas.

(*f*) With the pressures at .065 cm. and .032 cm., the glow extended out over half way to the plate and gauze, its exterior surface taking somewhat the outline of these two. There was now a reddish glow on the surface of the plate.

(*g*) At a pressure of .015 cm. there was a glow throughout the whole tube, except for a curved dark space near the middle of the volume.

(*h*) At a pressure of .0088 cm. and up to the limit when the discharge would no longer pass, the tube was filled with light of a bluish tinge, with a whitish glow on the point; and the discharge was intermittent.

The negative discharge at the low pressures was for the most part intermittent, and a few peculiarities only will be noted.

At a pressure of 2.5 cm. there was a considerable time interval between the application of the voltage (storage cells being used) to the point and the beginning of the discharge, being at times as much as eight minutes. When a glass tube containing one gram of one per cent. radium bromide was placed near the tube, however, the discharge always commenced immediately on applying the voltage.

At a pressure of .9 cm. a reddish spot of light, five to eight millimeters in diameter, appeared on the extreme edge of the wire gauze, with a corresponding spot on the point opposite. These spots of light rotated irregularly about the axis of the tube keeping more or less together. They seemed to be part of an arc discharge. At lower pressures down to .19 cm. these spots became more and more extended and diffused, finally appearing to envelop the whole point and gauze cylinder.

At the lowest pressures at which the negative discharge would pass its appearance was that of a diffused light throughout the whole space, being somewhat more intense at the surface of the point electrode.

General Remarks.

14. It is of some interest to compare the potentials required to start a discharge from the three classes of points which have been studied. Such a comparison is made in Figs. 5 and 6, where, under the potential-diameter curves for $C = 0$, are drawn in broken lines the corresponding curves for needle points (taken from Figs. 2 and 3), and for cylindrical wires (taken from Figs. 2 and 5 of the previous paper — loc. cit.).

The comparison shows how much easier it is to start a current from the cylindrical wires than from the other points of like diameter. And while much finer needle points can be obtained than the diameters of the smallest wires, still the discharge from the fine wires takes place at considerably lower voltages than it does from the finest needles. The wires are preferable, too, because the fine needle points become blunter with use, while the wires of necessity do not. The formation of oxides on steel points, especially during the positive discharge, is also a disadvantage.

For the sake of comparison, the formulæ which have been found to represent best the experimental results for the positive currents from all of the points tried in each of the different cases, are here brought together. The distance between the point and the plane was 1.5 cm. in each case.

$C = 2.58 \times 10^{-13}(1 + .110d)\, V(V - M)$ for cylindrical wires with hemispherical ends.

$C = 2.60 \times 10^{-13}(1 + .30d)\, V(V - M)$ for cylindrical wires with plane ends.

$C = 2.58 \times 10^{-13}(1 + .319d)\, V(V - M)$ for steel needle points.

$C = 2.49 \times 10^{-13}(1 + .176d^3)\, V(V - M)$ for 12° conical points.

The values of the minimum potentials (M) in the four cases are given in turn by, $755 + 5{,}465d$; $705 + 5{,}670d$; $2{,}590 + 4{,}750d$; and $1{,}980 + 5{,}200d^{\frac{1}{2}}$.

The initial constants in the current formulæ are quite alike, but there is much variation in the way that the current and the minimum potential depend upon the diameter of the point. The range of diameters used was different for the different cases and so the limits over which the formulæ have been tested are not alike.

The beginning of a discharge from a point and the smaller currents from it, are often subject to considerable irregularity, especially if the discharge is negative. Some irregular resistance is present in these cases on the surface of the point, due perhaps to a condensed layer of gas on the metal surface hindering the free passage of the ions to and from the surface. The exposure of the point to radiations, like those from radium, removes the irregularity completely in some cases and partly so in other cases. It may be that the ions formed by the radiations in the condensed layer, moving under the action of the strong electrostatic field, are able to break up this surface layer more or less completely.

There is much less trouble with the larger currents from the point, possibly because the heat generated by the discharge dissipates the gas layer. Nevertheless when a large negative current from a point is reduced to a small value the irregularities become more pronounced than before and often a higher voltage is now required to start the current than was necessary in the first place.

This applies to the brass and steel points used in these experiments, and it is possible that some new effect is added due to an oxidation of the point or some other condition produced by the heating effect of the discharge. Users of platinum points have found, on the contrary, that often the potential at which a current stops is smaller than that at which it began, and hence in this case the gas layer may have been removed by the discharge and no new resistance introduced.

The reason why the positive discharge is on the whole so much more regular than the negative, may be due to the greater facility with which the smaller negative ions, produced by collision outside of the gas layer, penetrate the condensed layer and get to the metal surface.

The value of the minimum potential has been taken throughout as the lowest potential at which a current could be detected flowing from the point. The points have in all cases been exposed to the radiation from radium, and the potential at which a positive current was first observed to begin, as the voltage was gradually increased, was the same as that at which the current ceased, as the voltage was diminished. The smallest difference of potential that could be observed with the voltmeter used was about 25 volts.

When the results for the negative discharge were not completely consistent, it was deemed advisable to use for the purpose of calculation those which showed the current to flow most easily, as they were the most free from the disturbing resistances which have been discussed. As already stated these results were those that were first taken with the point, before it had been used with large currents.

A formula, such as has been used to represent the potential-current curves, assuming as it does a gradual increase in the current from the beginning, as the voltage is raised, is better adapted to represent results for the simplest conditions obtaining at a point, than does one where a discontinuous rise of current at the start is assumed.

Summary.

15. (*a*) Results are obtained from which it is possible to find the current that would flow in dry air to a plane 1.5 cm. distant, from points of any diameter, at any potential, when these points are either steel sewing needles of the usual taper, or 12° cones.

(*b*) The potential required to start a discharge from a point of any diameter and the current flowing from any point at any potential, can each be represented by a formula, for the positive discharge from either of the two kinds of points mentioned.

(*c*) The potential required to produce a current from the finest needles or cones, is considerably greater than is necessary when fine cylindrical wires are used.

(*d*) Masses of iron oxide form at the tips of steel needles during the positive discharge from them, and to a much less extent during the negative discharge.

(*e*) The negative discharge from the points shows considerable irregularity, especially for the smaller currents.

(*f*) The current flowing to a spherical surface from a point placed at its center of curvature distributes itself quite uniformly over the whole surface of the hemisphere opposite.

(*g*) With diminution of pressure the discharge between a point and a plane (distance = 1 cm.) takes place at gradually lower and lower potentials, and the current increases more and more rapidly with change of voltage. Below a pressure of one centimeter the

potential required for the discharge drops rapidly to about 400 volts as the pressure is reduced to a few hundreths of a centimeter, and then at about a hundredth of a centimeter it begins to increase again rapidly.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
November 8, 1907.

THE FLUORESCENCE AND ABSORPTION OF ANTHRACENE.

By Louise Sherwood McDowell.

ANTHRACENE, because of its intense blue-violet fluorescence, offers a promising opportunity for the comparative study of the fluorescence of a substance in its different forms: solid, liquid, and solution. The present study was undertaken, in order to make such a comparison, at the suggestion of Professors Nichols and Merritt, of whose inspiring interest the author wishes to express her grateful appreciation. Owing to the impurity of the anthracene used, the work naturally fell into three divisions: (1) the study of the fluorescence of impure anthracene; (2) the purification of the anthracene; (3) the study of the fluorescence of pure anthracene.

Nature of Anthracene.

Anthracene is a benzene derivative, prepared from those portions of coal tar which boil between 340° and 360° C. In its pure form the anthracene crystallizes in monoclinic plates, and has a blue-violet fluorescence. It melts at 213° C. and boils at 351° C. The crude anthracene contains an impurity of unknown composition, chrysogen, the slightest trace of which has been supposed entirely to destroy the blue-violet fluorescence.

History.

No study of the fluorescence of the crude anthracene has, so far as the writer is aware, yet been undertaken. The study of the fluorescence of the pure anthracene has been chiefly confined to the solutions. In this field, the work of two men needs to be mentioned, J. Hartley, in England, and O. Knoblauch, in Germany. Hartley[1] studied the absorption bands of solutions of pure anthracene in glacial acetic acid diluted with absolute alcohol. The solutions varied in concentration from 1 part of anthracene in 1,000 of the

[1] Hartley, J., Journal Chemical Society, 39, 162.

solvent to 1 part in 50,000,000. He found four absorption bands in the following positions: $\lambda.3600$–$.3607\,\mu$; $.3430$–$.3434\,\mu$; $.3285$–$.3287\,\mu$. The least refrangible was not measurable on his scale.

O. Knoblauch,[1] in a general study of the intensity of fluorescence of various solutions, studied ten solutions of pure anthracene, which he arranged in order of intensity of fluorescence, as follows: benzol = toluol = xylol = isobutyl alcohol > amyl alcohol = ethyl alcohol = ether > acetone > petroleum ether > chloroform.

In this country E. L. Nichols and E. Merritt,[2] in a study of the fluorescence and phosphorescence of various organic substances at low temperatures, have found that, at the temperature of liquid air, the solid still shows the characteristic blue-violet fluorescence unchanged in intensity, and also a white phosphorescence.

Within the past year, T. S. Elston[3] has made a study of the fluorescence of the vapor of pure anthracene and found that the fluorescence spectrum extends from $\lambda.365$ to $.470\,\mu$, with bright bands at $\lambda.390$, $.415$, and $.432\,\mu$, and that the absorption spectrum extends continuously from about $\lambda.400\,\mu$ to some point beyond $\lambda.325\,\mu$.

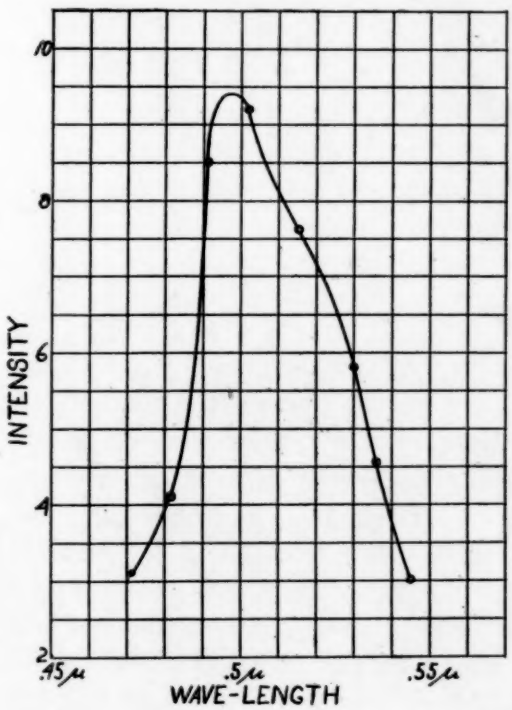
FLUORESCENCE OF IMPURE ANTHRACENE.

The present experiments were begun with a partially purified, crystallized anthracene, yellow in color. This showed a bright green fluorescence. To put in convenient form for photographing, the anthracene was melted between two microscope slides, and allowed to cool. The layer so formed was about a millimeter in thickness. In this form the anthracene showed three distinct absorption bands, the position of which was found photographically. The plate was placed close to the tube of the spectrograph; the carbon arc light focused upon it; and an exposure of ten to twelve seconds made. Of the five exposures on each plate, the first and fifth were of the potassium and strontium arcs respectively. By means of these two reference spectra, a calibration curve was plotted, and the position of the absorption bands read from the curve. See plate at close of article. The bands were found to have the following positions:

[1] Knoblauch, O., Wiedemann's Annalen, 54, 192.
[2] Nichols and Merritt, PHYSICAL REVIEW, 18, 355.
[3] T. S. Elston, Astrophysical Journal, April, 1907.

Extent.	Middle Point.
λ	λ
4,990–4,870	4,930
4,620–4,520	4,570
4,215–	

For the fluorescence, the mercury arc lamp of the Arons Lummer type was used as an exciting light, and also as a reference spectrum. The first four exposures on each plate were of the fluorescence spectrum, for which the apparatus was so arranged that the spectrograph and lamp were at right angles and the plate placed with its



edge vertical and directly in front of the slit of the spectrograph. For the fifth exposure, the light of the mercury arc was reflected directly into the spectrograph by a glass mirror placed at an angle of 45°. The time of exposure varied, according to the width of slit, from five minutes to an hour. In order to test the effect of the glass, one photograph was taken in which the plate was replaced by a solid cylinder of anthracene about .8 cm. in diameter; and the

light from the mercury arc was passed through a violet glass to cut off the green light. The resulting photographs show two fluorescence bands, of which the first is but faintly visible in the photograph, although it appears to the eye the more intense. See plate at close of article. The position of the bands is:

	λ
Band I.	5,440–5,250
Band II.	5,145–4,865

A photograph of the fluorescence of solid methyl anthracene taken in the same way showed these two green bands, and in addition a faint blue fluorescence extending to line .4358 μ of the mercury spectrum.

As a check upon the results obtained photographically, the intensity curve for the green fluorescence bands was taken by means of a Lummer-Brodhun spectrophotometer. The iron spark was used as an exciting light. In order to avoid stray light, the visible portion of the spectrum, formed through a quartz lens and prism, was intercepted by a screen, and only the ultra-violet rays allowed to fall upon the plate of anthracene. In this case the plate was formed by subliming the anthracene on glass. As a comparison light there was used an acetylene flame reflected at an angle of about 45° from a block of magnesium carbonate. To prevent light from this source falling on the plate the acetylene flame, except for the circular opening through which light fell upon the reflecting surface, was completely enclosed by a black screen. The results are shown in the accompanying curve. To test the killing effect of the extreme red and infra-red rays upon the green fluorescence, the light of the arc lantern was intercepted by a thin rubber screen, and the rays which passed through allowed to fall at grazing incidence upon the fluorescing surface. The intensity of the fluorescence as observed through the spectrophotometer remained unchanged.

For the determination of the rays which excite the green fluorescence of the solid, the spectra of the carbon arc lamp, the mercury arc, the Nernst glower, and the iron spark, were successively thrown on a screen, and the plate of sublimed anthracene moved slowly through the spectrum. In the last case, the spectrum was produced by a quartz lens and prism, to avoid the absorption

due to glass. The results show that, with the possible exception of two narrow bands in the blue, all rays are effective from the green to the extreme ultra-violet.

The study of the fluorescence of the liquid anthracene involved several difficulties. The anthracene, if melted too rapidly, decomposes; also it begins to sublime at temperatures far below the melting point, and if removed from the heat, coats over the surface before an observation can be taken. To obviate these difficulties, the anthracene was placed in a long glass tube about one and one half centimeters in diameter, and placed in an electric heater, $6 \times 6 \times 1$ in. The whole was covered with asbestos paper, except for openings through which the tube and thermometer were received, the light admitted, and observations taken. For the absorption bands, both a gas flame and a focused carbon arc were used, but no absorption bands were visible through the spectroscope. Throughout the experiment, the thermometer was kept only a few degrees above the melting point, yet the solution under the influence of the heat rapidly decomposed, turned orange, and then dark brown until it became almost opaque to light. For the fluorescence the plan was first tried of sealing the metal terminals for a spark into the glass tube, but the anthracene vapor attacked the terminals and caused them to burn out so rapidly that the plan had to be abandoned. Thereafter the spark was placed just outside the glass tube. Under these conditions, the liquid showed no fluorescence when excited by the spark between terminals of aluminum, zinc, tin, or iron, by the mercury vapor lamp, or the carbon arc.

To test the fluorescence of impure anthracene in solution, the following solvents were used: benzol, toluol, xylol, isobutyl alcohol, amyl alcohol, ethyl alcohol (absolute), ether, acetone, petroleum ether, chloroform, carbon disulphide, and glacial acetic acid. Concentrated solutions were first made and then diluted in the ratios 1:2, 1:4, 1:8, 1:16, 1:32. In ether and acetone solutions, through cells three centimeters thick, there were visible very faint absorption bands, too faint to affect the photographic plate when exposures for 25 minutes were made. In this case the light was that of the ordinary gas burner. No fluorescence was observable under any of the excitations previously tried. In testing the exciting powers

of the ultra-violet rays small rectangular glass cells 5.65 × 3 × 1 cm. (inside measurement) were nearly filled with the solution to be tested; the open top covered by a quartz plate; and the metal sparks of aluminum, zinc, tin, iron, and copper successively placed above. In no case was fluorescence visible.

PURIFICATION OF ANTHRACENE.

In the course of the determination of the exciting rays, an attempt was made to use plates prepared by evaporating a chloroform solution on glass. When a plate so prepared was held in the ultra-violet spectrum of the iron spark it fluoresced, but with a faint blue color, suggestive of pure anthracene. A similar test of other solutions, which had been standing in a dimly lighted room for several days, gave the following results:

Chloroform	blue.
Xylol	blue-violet.
Isobutyl alcohol	blue-green in center, blue on edge.
Toluol	blue-green.
Amyl alcohol	green.
Absolute alcohol	green.
Acetone	green.
Ethyl ether	green in center, blue on edge.
Glacial acetic acid	green in center, blue on edge.
Benzol	green in center, faintly bluish green on edge.
Carbon disulphide	green in center, faintly bluish in spots, usually yellowish white, non-fluorescent on edge.
Acetone	yellowish green in center, faintly blue-green or green on edge.

Obviously the next step was to decide the relative effects of solvent, concentration, light, and time, in producing the change. For this purpose fresh solutions, saturated and dilute, were made in the most promising solvents: chloroform, xylol, and isobutyl alcohol. Portions of these solutions were left in diffuse daylight and in a photographic dark room. Each day for a week, tests were made by evaporating small portions on glass and placing the evaporated product in the light from the carbon arc, and also from the iron spark. The tests showed:

I. That daylight assists the change although bright sunlight is not essential.

II. That solvents differ in their ability to produce the change, *i. e.*, xylol is better than chloroform.

III. That a difference in concentration has little effect upon the change.

IV. That the time required depends upon the brightness of the light and the solvent used.

V. That in some cases the evaporated product, if exposed to air, decomposes.

These results led to a study of the method of Fritzsche,[1] who was probably the first to undertake the purification of anthracene. His method in brief was this: The crude anthracene was dissolved with heat in a mixture of coal-tar oils (Steinkohlenoel) and placed in the sunlight. The substance which first crystallized out was dissolved in the same way until crystals of the desired purity were obtained.

Berthelot's[2] method is similar. The coal-tar product left in the retort by the distillation of the substances which boil below 350° is crystallized again from boiling xylol, and each time the part which crystallizes out on cooling, is pressed out. Then it is again crystallized from alcohol, and finally sublimed at the lowest possible temperature.

In the first experiments performed by the writer, the impure anthracene was dissolved in boiling kerosene, and the saturated solution allowed to stand in sunlight until a portion crystallized out. These crystals were redissolved in fresh kerosene, and the process repeated until the product was very nearly pure white. After the last filtration, the anthracene was washed in cold alcohol, in which it is but slightly soluble. To test the effect of the fresh kerosene, the product which first crystallized out was redissolved in the same solution, allowed to crystallize out a second time, and the process repeated until the yellow color disappeared. The precipitate was finally filtered out and washed as before. No difference in the product so obtained was observable. As a third test, the hot solution of anthracene was kept in the sunlight for fifteen minutes, at a temperature which prevented crystallization; then allowed to crystallize; filtered out, and the precipitate washed in alcohol. Since this product when subjected to the tests described below showed

[1] Fritzsche, Zeitschrift für Chemie, 1867, p. 290.

[2] Berthelot, Bulletin de la Société Chimique de Paris, 8, 232.

the greatest purity of all the kerosene treated products, it is evident:

I. That renewal of solvent is unessential.

II. That repeated crystallization is unessential.

The same method was tried with chloroform and xylol. An attempt to substitute arc light for sunlight showed that owing to the lessened intensity of the light a much longer time was required.

To the products thus purified, various tests were applied. They were found to possess a blue-violet fluorescence, and to dissolve readily in any of the solvents used, giving solutions with a blue-violet fluorescence. The xylol and chloroform products, if not carefully washed, gradually lost their fluorescence and turned a yellowish brown. Sublimation of the products in air showed that the chrysogen was still present, for the sublimate gave in one spot blue-violet fluorescence; in another, green. When the sublimation was gentle, that which was first deposited on the cold plate of glass showed blue-violet fluorescence. As the heat increased the later deposit showed green fluorescence, so that, by illuminating the plate from the one side or the other, the blue-violet or the green fluorescence was obtained. By stopping the gentle sublimation at the proper time, a product was obtained which gave only blue-violet fluorescence, while the rapid sublimation of the residue gave a product of which the green fluorescence was more intense than any yet observed. Apparently by this means there was secured a greater concentration of the chrysogen, although a complete separation was not effected.

To test whether the change in color of the fluorescence was due to the heat to which the product was subjected, the blue-violet sublimate was rapidly resublimed and gave still a blue-violet fluorescence, which grew gradually fainter as the amount of the sublimate was lessened by repeated sublimations. To complete the separation of the pure anthracene the kerosene-treated product was sublimed in a partial vacuum. The crystals were placed in the bottom of a cylindrical tube. About two inches above was a wire triangle, upon which rested a small glass plate. The tube was connected to a mercury pump and exhausted as far as possible, then closed and placed in a bath of salt and water maintained approxi-

mately at 109° C. The sublimation was allowed to continue for about two hours, then the plate was removed and tested. By this means regular crystals of pure anthracene were obtained, and in the later fractions somewhat irregular fern-like crystals, the form of which was apparently modified by the presence of the chrysogen. Complete separation of the chrysogen was not effected. An attempt to separate the pure anthracene by sublimation, before treatment with the kerosene, proved unsuccessful.

To account for these results one possible explanation suggested itself, an explanation based upon the following known facts:

I. Anthracene, if allowed to stand in solution in the bright sunlight, gradually goes over into dianthracene ($C_{28}H_{20}$), which melts at 244° C., but upon melting reverts to anthracene, the melting point of which is 213° C.

II. Chrysogen is known to go through an apparently similar transformation, since if ordinary white dianthracene, which has a blue fluorescence, is melted, the resulting product is yellow and fluoresces bright green.

May it not be that, when the anthracene is exposed to sunlight, the chrysogen first goes over into dichrysogen so that the product which crystallizes out is a mixture of anthracene and dichrysogen, and that the latter upon sublimation at high temperatures reverts to chrysogen and thus restores the green color? This would explain the greater ease of separation after the product is crystallized out of solution.

The Fluorescence and Absorption of Pure Anthracene.

In the study of the fluorescence of the solid, a comparison was made of the fluorescence of the original yellow anthracene, the bright green product of rapid sublimation, the blue-violet product of gentle sublimation, and the pure anthracene crystals from the sublimation in vacuo. As exciting lights, the mercury arc and the ultra-violet rays of the iron spark spectrum were used. As before, the method was photographic. For the absorption bands, the light of the carbon arc lamp was focused upon the plates as in the case of the impure anthracene. For the iron spark excitation the ultra-violet rays were allowed to fall on the plate, and the visible spectrum intercepted by a screen.

Tables I. and II. give the results of the comparison. A question mark in a column indicates that owing to the presence of a mercury arc line, the exact position of the band is uncertain. The last two bands are those obtained for the fluorescence of the impure anthracene. These results indicate that the substance is fluorescent in all stages of the purification, and that the blue-violet fluorescence is not entirely killed by the presence of the chrysogen. In the purer

TABLE I.

Fluorescence of Solid Anthracene of Different Degrees of Purity.

Substance.	Time.	Bands.					Extent.	Excitant.
G.S.	30 min.	?			5,010	5,310	4,860-5,370	M.A.
O.S.	30 "	4,358			5,010	5,310	4,130-5,370	"
B. + G.	45 "	4,358			4,985	5,310	4,130-5,370	"
V.B.	90 "	4,358		4,730	4,985			"
G.S.	45 "				4,975	5,280	4,850-5,375	"
B. + G.	90 "	4,358			4,980		4,140-5,080	"
G.S.	75 "	4,250	4,510	4,750	4,960		4,190-5,060	U.V.
O.S.	60 "	4,260	4,490	4,750	4,980		4,190-5,090	"
V.B.	120 "	4,260	4,490		4,960		4,190-5,030	"
B. + G.	60 "	4,260	4,510		4,960		4,190-5,060	"
P.A.	120 "	4,220	4,470				4,100-4,750	"
O.	120 "				4,940		4,870-5,010	"

TABLE II.

Position of Absorption Bands of Solid Anthracene.

Substance.	Time.	Width of Bands.		
O.S.	12 sec.	4,090-	4,840-4,900	4,540-4,615
G.S.	20 "	4,090-	4,860-4,925	4,570-4,650
B. + G.	20 "	4,090-		
V.B.	25 "	4,100-		
V.B.	25 "	4,100-		

G.S. = green sublimate.
O.S. = original anthracene sublimed.
B. + G. = blue and green sublimate.
P.A. = crystals of pure anthracene.
O. = original anthracene melted on glass.
V.B. = violet-blue sublimate.
M.A. = mercury arc.
U.V. = ultra-violet rays of iron spark.
Arc = carbon arc through glass.

specimens, however, the violet fluorescence was relatively strong, the green weak, and in the most impure products, the violet was so faint as to be barely visible. See plate.

For the study of the absorption and fluorescence of the solutions of pure anthracene, the kerosene-treated product was used. Small amounts of concentrated solutions in the following solvents were made, and diluted as described later: xylol, benzol, toluol, isobutyl alcohol, amyl alcohol, ethyl alcohol (absolute), ether, acetone, petroleum ether, chloroform. To test the effect of varying concentration upon the position of the fluorescence bands, the fluorescence bands of the xylol solutions with six different concentrations from $\frac{1}{4}$ to $\frac{1}{512}$ conc. were photographed. There was found to be no apparent shift of the bands with the concentration. The absorption bands of each solution in turn were then photographed, in the following way: The light of an acetylene flame was diffusely reflected from a block of magnesium carbonate at 45°; the solution to be tested was placed, in a glass cell 1 cm. in thickness, in the path of the reflected beam, and the spectrograph placed in contact with the cell. All direct light was shut off by a screen. As in other cases, the mercury arc spectrum was used for reference. As an additional precaution against shift with concentration, only dilute solutions were used, the solution in most cases probably being not more than $\frac{1}{250}$ conc. After each exposure, the solution was replaced by the plain solvent in a similar cell, and another exposure made in the same way. Table III. gives the results. The dash indicates that the band extends to the violet end of the visible spectrum.

For the fluorescence bands, the arc light was used. The mercury arc, and sparks of iron, copper, zinc, tin, lead, aluminum, cadmium, antimony, bismuth, silicon, and carbon, failed to give an exciting light sufficiently intense, even when placed directly above the cell at a distance of one inch, and separated from the solution by a quartz plate. In order to guard against the possibility of stray light, the cell was covered with black paper except for two opposite rectangular slits about 1 cm. wide, through which the beam of exciting light passed, and for a small circular opening at right angles to these and just fitting the lens of the spectrograph. Also the barrel of the spectrograph was covered with black paper, and

TABLE III.

Position of Absorption Band of Pure Anthracene in Solution.

Solvent.	Time.	Bands.
Xylol $\frac{1}{16}$ conc.	5 min.	4,080–
Xylol $\frac{1}{32}$ "	5 "	4,080–
Xylol $\frac{1}{64}$ "	5 "	4,080–
Xylol $\frac{1}{128}$ "	5 "	4,050–
Xylol $\frac{1}{256}$ "	5 "	4,050–
Xylol $\frac{1}{512}$ "	5 "	4,050–
Benzol	5 "	4,050–
Toluol	5 "	4,050–
Isobutyl alcohol	5 "	4,050–
Amyl alcohol	5 "	4,050–
Absolute alcohol	5 "	4,050–
Ether	5 "	4,050–
Acetone	5 "	4,080–
Petroleum ether	5 "	4,080–
Chloroform	5 "	4,080–

TABLE IV.

Position of Fluorescence Bands of Pure Anthracene in Solution.

Solvent.	Time.	Bands.				Extent.
X. $\frac{1}{4}$ c.	60 min.	4,050	4,270	4,520		5,030–4,000
X. $\frac{1}{8}$ c.	70 "	4,050	4,270	4,520		5,030–4,000
X. $\frac{1}{16}$ c.	60 "	4,050	4,270	4,520		5,140–4,000
X. $\frac{1}{32}$ c.	60 "	4,060	4,300	4,570		4,970–4,000
X. $\frac{1}{64}$ c.	60 "	4,060	4,300	4,570		5,030–4,000
X. $\frac{1}{128}$ c.	60 "	4,060	4,300	4,570		4,970–4,000
X. $\frac{1}{256}$ c.	60 "	4,060	4,310	4,555		5,030–4,000
B.	60 "	4,060	4,310	4,570		5,030–4,000
T.	60 "	4,050	4,285	4,540		4,970–4,000
I.A.	60 "	4,030	4,260	4,540	?	4,970–4,000
A.A.	60 "	4,030	4,250	4,500	4,810	4,970–4,000
Ab.A.	60 "	4,020	4,260	4,500	4,760	5,030–4,000
E.	60 "	4,035	4,225	4,535	4,860	5,030–4,000
A.	60 "	4,040	4,250	4,535	4,860	4,980–4,000
P.E.	60 "	4,030	4,225	4,490	4,800	4,900–4,000
C.	60 "	4,050	4,260	4,550		4,890–4,000
X.	50 "	4,060	4,290	4,585		4,900–4,000
T.	50 "	4,050	4,270	4,550		4,900–4,000
X.	60 "	4,050	4,290	4,535		5,000–4,000

X. $\frac{1}{4}$ c. = xylol $\frac{1}{4}$ conc.
B. = benzol.
T. = toluol.
I.A. = isobutyl alcohol.
A.A. = amyl alcohol.
Ab.A. = absolute alcohol.
E. = ether.
A. = acetone.
P.E. = petroleum ether.
C. = chloroform.

had a black screen encircling it at a distance of about two inches from the cell, to prevent any possibility of reflected light entering the instrument.

Of the five exposures made on each plate, the first and third were of the fluorescing solutions, the second and fourth of the plain solvents, the fifth of the mercury arc. As was to be expected, the photographs of the plain solvents were almost blanks, showing the nearly total absence of stray light. In order to determine the exact position of the fluorescence bands, a calibration curve was drawn from the position of the mercury lines. Table IV. gives the results. The mid-point of each band and the total extent of the fluorescence are given in each case. A question mark indicates that the presence of bands in that column is doubtful. For the last exposure the iron arc was used as an exciting light. Otherwise the procedure was the same. See plate.

There was found to be no shift in the position of the bands either with a change in concentration or solvent. Table V. gives the average wave-lengths for the different bands of both pure and impure anthracene in the three forms. The figures for the vapor are those given by T. S. Elston.

TABLE V.

Average Position of Fluorescence Bands.

Solid.	4,250	4,495	4,745	4,980	5,300
Solution.	4,050	4,275	4,540	4,820	
Vapor.	3,900	4,150	4,320		

The fluorescence bands occur, apparently, at equal intervals, with a distance between bands approximately equal to .025 μ. With the change from solid to solution and solution to gas, there is a shift in the bands towards the shorter wave-lengths.

SUMMARY.

The results of the study may be briefly summarized thus:

I. Commercial anthracene, in the solid form, possesses a fluorescence fully as intense as pure anthracene, but different in color. It consists of bright bands at .498 μ and .530 μ. The absorption spectrum consists of bands in the positions λ.499–.487 μ, .462–.452 μ, and of a continuous spectrum from λ.4215 μ to some point beyond the range of the apparatus.

II. The blue fluorescence is not entirely destroyed by the presence of the chrysogen, but may with the proper excitation coexist with the green fluorescence.

III. The fluorescence of the pure anthracene, both solid and in solution, consists of distinct bands separated by regions of diminished intensity.

IV. In the case of the solid, there are three bands at $\lambda.425\,\mu$, $.450\,\mu$, and $.475\,\mu$. In the case of the solution, there are three, possibly four, bands at $\lambda.405\,\mu$, $.4275\,\mu$, $.475\,\mu$, and (?) $.482\,\mu$.

V. With the change from solid to solution and solution to gas there is a progressive shift in the fluorescence bands towards the shorter wave-lengths.

VI. The absorption spectrum of the pure anthracene is continuous from about $\lambda.410\,\mu$ to some point in the ultra-violet beyond the range of the apparatus. That of the solution is continuous from about $\lambda.405\,\mu$.

Physics Laboratory,
Cornell University.

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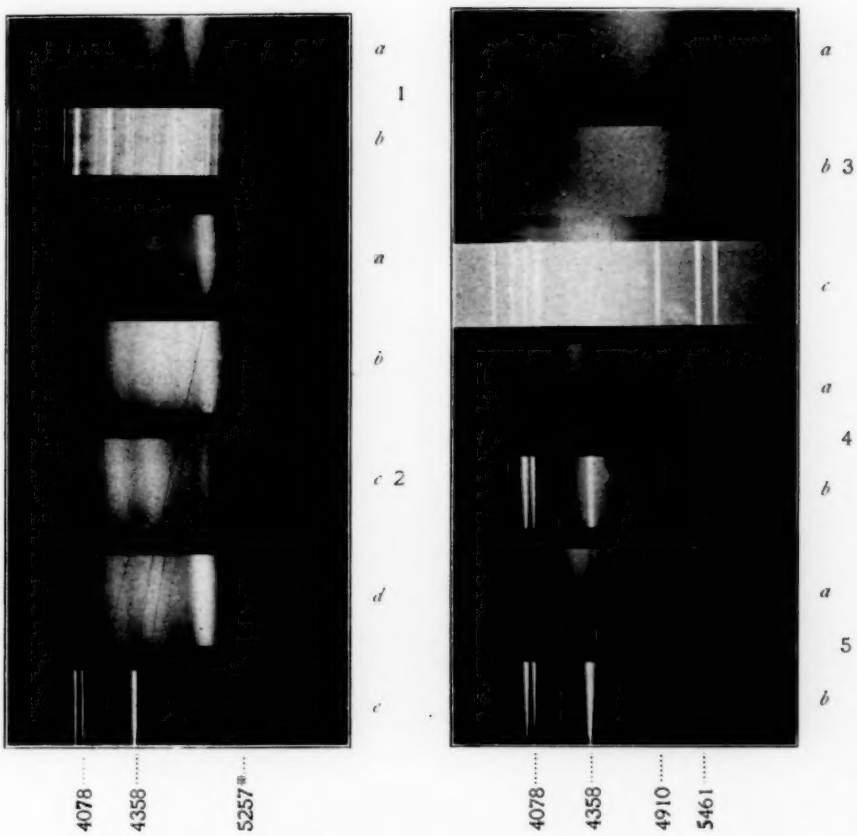


Fluorescence and Absorption Spectra of Anthracene.

1. *a*, Absorption of solid commercial anthracene; *b*, Strontium.

2. Fluorescence of solid anthracene of different degrees of purity (see Table I.): *a*, Green sublimate; *b*, Commercial anthracene sublimed; *c*, Violet-blue sublimate; *d*, Blue and green sublimate; *e*, Mercury arc.

3. *a*, Absorption of purified anthracene in solution; *b*, Plain solvent; *c*, Mercury arc.

4. *a*, Fluorescence of purified anthracene in solution, carbon arc excitation; *b*, Mercury arc.

5. *a*, Fluorescence of purified anthracene in solution, iron arc excitation; *b*, Mercury arc.

5257* is the wave-length of the strontium line at the extreme right.

THE HEAT DILUTION OF AQUEOUS SALT SOLUTIONS.

By F. L. Bishop.

THE following paper contains the description of a new method and form of calorimeter for certain thermochemical measurements: some determinations of the heat of dilution of solutions of sodium nitrate, potassium nitrate, potassium chloride, barium nitrate: and some conclusions on an analogy between this heat-quantity and the Joule-Thomson effect and on the application of van der Waals's equation to solutions.

Although many investigators[1] have already studied the heat of dilution of aqueous salt solutions, yet it seemed desirable to study more thoroughly solutions at moderately low concentrations: this work was undertaken with that end in view.

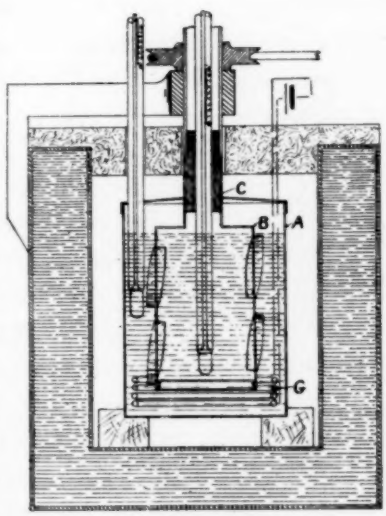


Fig. 1.

Calorimeters. — This consists of two concentric cylinders *A* and *B*, Fig. 1. The inner one is suspended by the tube *C* by which it is rotated at a constant rate. This tube was for a part of its length made of hard rubber to avoid undue heat conduction. Vanes on the inside of the outer calorimenter and on the outside of the inner cylinder provide ample means for mixing and agitating the liquids. The bottom of the inner calorimeter

[1] Among others reference may be made to the following: Thomsen, Thermochem. Untersuchungen, Vol. 3; Varali Thevenet, Cimento., 4, 186, 1902; Stacckelberg, Zeitschr. f. Phys. Chem., 26, 533, 1898; Rumelin, Zeitschr. f. Phys. Chem., 58, 461, 1907.

was made so that it could be easily removed. This was accomplished by turning down the bottom of the cylinder until its wall was very thin and would spring a small amount. The bottom was accurately fitted to this and forced into it slightly until the joint was water tight. It was found that the bottom could be easily removed by pressing down on it with the thermometer.

The two liquids are mixed by dropping the bottom out of the inner calorimeter and at the same time lowering it until its top is below the surface of the liquid. Then the liquid is forced by the rotary motion of the inner calorimeter to pass up the outside and down the inside of the inner calorimeter, or if the direction of rotation is reversed, it can be made to circulate in the opposite direction.

A small piece of thin metal, not shown in the drawing, just large enough to move freely in the inside calorimeter, was fastened to the thermometer thus preventing the liquid on the inside from taking up a regular rotary motion and causing it to be very completely agitated so that it would assume the temperature of the liquid on the outside. The calorimeters were made of brass and covered before each experiment with a thin coating of bees' wax. Three different sizes of calorimeters varying from 2,000 c.c. to1,000 c.c. for the outside and from 700 c.c. to 300 c.c. for the inside cylinder gave a number of ratios of solvent to solute. The calorimeter was placed in a double-walled vessel filled with water and covered with two layers of inch felt, and the whole arrangement was placed in a tank of oil[1] kept at a constant temperature.

The difference in temperature was measured by Beckmann thermometers which read directly to hundredths of a degree. Instead of determining the heat-capacity of the apparatus a difference of temperature nearly equal to that obtained in the dilution experiments was reproduced by means of an electrical heating coil *G*, Fig. 1, and the relation between rise of temperature and electrical energy expended was determined. A number of different forms of this heating coil were used. One was made by drawing a bare

[1] For a description of this constant temperature tank see A Method of Determining Thermal Conductivity, by F. A. Laurs, F. L. Bishop, and P. McJunkin, Proc. Am. Ac. of Arts and Sciences, Vol. XLI., p. 455.

german-silver wire into a capillary glass tube and then coiling it into the desired shape. Another and one of the most satisfactory was made by using small copper tubing and insulated wire. The input of electrical energy was measured by a Weston Laboratory standard ammeter and voltmeter and the time by a stop watch.

All the instruments used in the final readings were carefully calibrated, the thermometers had been compared by the Reichsanstalt, and the electrical instruments were compared with a Carhart-Clark cell by means of a potentiometer. Preliminary experiments were made to determine the best size of calorimeters to give the various quantities such magnitudes that they could be read to 0.1 per cent. with the exception of the temperatures, and the mean of these is in most cases approximately that.

This form of calorimeter reduces the error due to radiation to a minimum since there is only one calorimeter exposed to radiation. This error could be completely eliminated by causing the liquids to mix at a slower rate and supplying electrical energy at such a rate there would be no change of temperature. In the cases where heat is given out it is only necessary to cool the liquids by a suitable arrangement to the temperature existing before mixing and then applying the electrical energy to reproduce the same temperature. This method also avoids the necessity of determining the heat-capacity of the liquids and of the calorimeter and insures that the two liquids shall be at the same temperature when mixed.

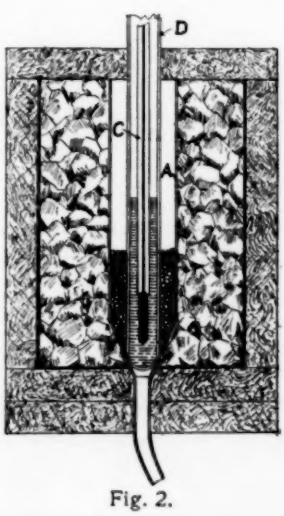


Fig. 2.

Tests of the Calorimeters. — In order to show that the electrical method gave the actual heat change when the liquids were mixed, certain metals whose heat-capacity are well known were investigated with the help of the apparatus shown in Fig. 2.

The apparatus consists of a vessel holding a certain amount of metal which is surrounded by a second vessel containing ice. The inner vessel has a conical bottom terminating in a short glass tube through which the metal falls

into the center of the calorimeter. This is closed by the glass tube *D* which also serves the purpose of holding a thermometer surrounded by mercury thus insuring that the metal in *A* is at the same temperature as the ice in the surrounding vessel. The whole is surrounded and covered by a double layer of felt.

This apparatus was placed over the calorimeter with the cone extending through the opening in the top of the outer part of the calorimeter in place of the thermometer. The inner cylinder was used without its bottom and with its top below the surface of the water so that it served simply to agitate the liquid.

A quantity of the metal was used which would give the same lowering in temperature as that given by mixing the liquids in the dilution experiments. This metal was allowed to stand surrounded by the ice until it was at the same temperature as the ice. Since the metals were reduced so much below the dew point it was necessary to dry the air surrounding the metal and to prevent the circulation of any fresh air around the metal by closing the outlet tube and covering the top. Meanwhile the water in the calorimeter was adjusted to constant temperature, after which the metal was allowed to pass into the water and the temperature and rate of radiation noted. Then the same temperature was reproduced by the electrical energy.

The six tests of the calorimeter made in this way are shown in the following table where column I. gives the metal used, II. the amount of heat as computed from the heat-capacity and the change in temperature of the metal, III. the amount of heat supplied electrically. The difference in the amount of heat shown for different tests indicates that different size calorimeters, were used. The first and second experiments should be considered as preliminary.

I.	II.	III.
Lead,	2,473	2,406
"	2,378	2,434
"	1,993	1,995
"	2,004	2,006
Copper,	2,295	2,285
Tin,	2,344	2,322

Results of the Experiments. — The solutions were prepared by weighing out the chemically pure dry substance, the concentration

being checked by evaporating to dryness a small portion of the resulting solution and weighing the residue. The substance as received chemically pure was recrystallized and tested for the ordinary impurities.

The following set of readings shows the character of the observations and indicates the change of the different quantities with the time during a run and the change in temperature due to radiation from which the correction for it was deduced. Readings of only one of the thermometers is here given. The readings were taken every minute. All the determinations were made at 25° C.

Run No. 16. *Potassium Chloride. July* 10, 1907. 2,192 *Grams of Solution, Concentration* 4.492. 294.2 *Grams of Water.*

Temperatures.			Amperes.	Volts.	Time in Seconds.
Before Mixing.	After Mixing.	After Applying Electricity.			
3.409	3.220	3.414	2.755	2.688	268.7
3.409	3.221	3.417	2.755	2.688	
3.409	3.222	3.417	2.754	2.687	
3.409	3.2225	3.417	2.752	2.685	
	3.2235	3.418	2.752	2.685	
	3.224	3.418	2.752	2.685	

Temperature decrease produced by mixing 0.192 corrected for radiation.
Temperature increase produced by electricity 0.194.
Resulting concentration 3.808 mols per liter of water.
Heat 48.71 calories per gram-mol.

In the following table of results column I. gives the amount of the solution in grams; II., the concentration of this solution in gram-molecular weights in 1,000 grams of water; III., the weight of water added; IV., the concentration of the resulting solution; V., the decrease of temperature corrected for radiation, when the solution was diluted; VI., the increase of temperature when the electrical energy was applied; VII., the electrical energy used in joules; VIII., heat in calories per gram-molecule of salt attending the change in concentration shown by columns II. and IV.; IX., the total heat absorbed when that quantity of solution containing one mol was diluted from the highest concentration to the concentration in question.

Potassium Nitrate.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
2,240	2.380	284.3	2.049	0.270	0.260	2,212	129.9	129.9
2,110	2.028	305.1	1.750	0.215	0.200	1,664	119.1	264.1
1,682	2.380	826	1.550	0.572	0.547	4,410	341.1	341.1
2,054	1.750	287.1	1.500	0.181	0.193	2,341	116.9	381.0
2,035	1.500	303.0	1.280	0.140	0.136	1,192	110.2	491.2
813	1.576	1,031	0.637	0.315	0.309	1,802	397.5	743
797	1 578	1,505	0.493	0.289	0.273	1,991	462.9	808
330.2	2.380	1,908	0.291	0.331	0.331	2,455	920	920
				Sodium Nitrate.				
828	2.172	312.0	1.500	0.305	0.225	887	189.2	189.2
842	2.172	314.8	1.510	0.305	0.244	961	185.1	185.1
769	1.500	305.1	1.040	0.174	0.174	711	165.8	355.0
334.5	2.172	752	0.593	0.331	0.269	1,058	507	507
305.7	1.500	747	0.400	0.177	0.179	822	404.7	594
314.2	1.510	747	0.409	0.175	0.174	685	392.0	581
				Barium Nitrate.				
792	0.705	291	0.506	0.068	0.078	347	144	144
827	0.705	291	0.510	0.078	0.077	277	138	138
819	0.705	300	0.503	0.053	0.061	257	153	153
776	0.506	295	0.360	0.040	0.036	173	128	170
801	0.510	302	0.286	0.044	0.043	271	191	329
301	0.705	756	0.191	0.075	0.070	312	409	409
297	0.506	751	0.137	0.043	0.077	347	306	450
				Potassium Chloride.				
2,190	4.492	296.0	3.804	0.182	0.198	1,612	48.0	48.0
2,192	4.492	294.1	3.808	0.192	0.194	1,521	48.7	48.7
1,690	3.804	284.6	3.127	0.179	0.181	1,185	55.8	103.8
1,595	3.127	286.5	2.564	0.124	0.130	836	47.1	150.9
1,498	2.564	305.0	2.053	0.102	0.115	718	46.1	197.0
1,496	2.053	297.5	1.670	0.075	0.072	473	44.1	241.1
342.0	4.492	1,456	0.673	0.256	0.263	1,845	372.6	372.6
338.1	4.492	1,456	0.666	0.254	0.232	1,683	384.8	384.8
338.3	4.492	1,862	0.218	0.217	0.538	1,876	395.7	395.7
796	1.461	285	0.058	0.070	1.05	318	60.0	306
776	1.05	293	0.036	0.050	0.74	231	53.0	358
310	1.461	762	0.062	0.067	0.39	318	173	418

The last three results given in this series of readings were obtained at the Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology with apparatus different except in design from that used in the other readings. The values for those

in the last column are of course interpolated from the other results. This not only tends to show that the results are free from instrumental errors but that the break in the curve of potassium chloride is due to some chemical change taking place in the solution. It is probable that other substances would show this same effect if greater differences of concentration had been used.

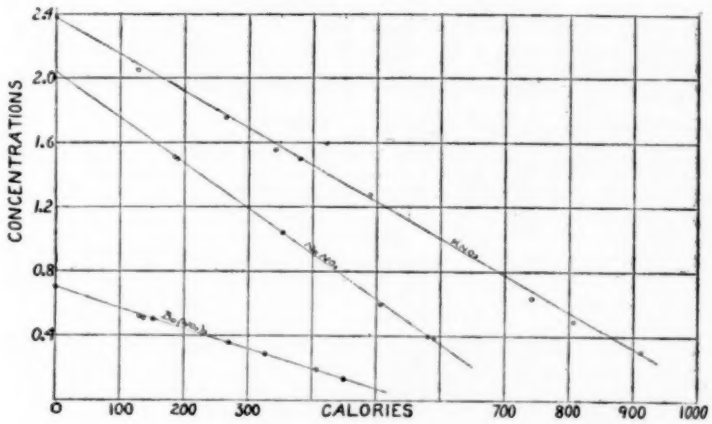


Fig. 3.

The results are represented graphically in Figs. 3 and 4. The ordinates show the concentrations, and the abscissa the total heat absorbed when that quantity of solution containing one mol was diluted from the highest concentration (that represented by the intercept of the curve on the ordinate axis) to the concentration in question.

Conclusions. — It is evident from these results that the value of dU/dc is a constant within the limits of concentration here shown if we represent by U the heat in calories per gram-molecular weight and by c the concentration of weight normal solutions. This corresponds to the fact that as the concentration approaches zero the heat effect produced by the addition of a definite amount of solvent dv to the solution approaches zero.

The fact that $dU/dv = a/v^2$, where a is a constant would seem to show that there is a similarity between the heat of dilution of a solution and the Joule-Thomson effect in gases for which as is well known, the same expression holds true.

This result would indicate that the osmotic pressure P, like the gas pressure in van der Waals's equation, must be corrected by a term a/v^2 representing the attraction of the molecules. The product Pdv would then represent the external work done when the volume of the solution is increased under the osmotic pressure P by the

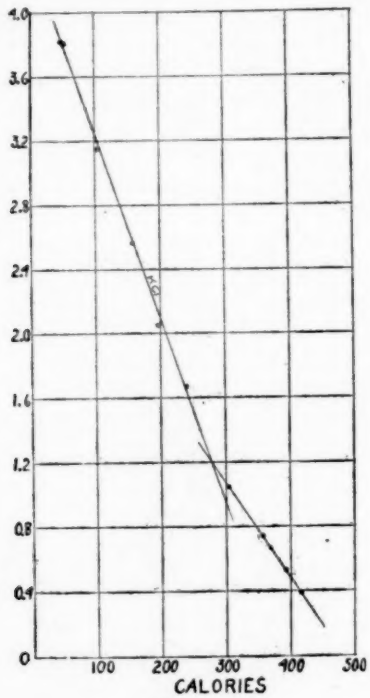


Fig. 4.

volume dv and the term $(a/v^2)dv$ would represent the internal work done in overcoming the attraction, which is equivalent to the heat of dilution.

I take this opportunity to thank Professor A. A. Noyes for placing a room and equipment of the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology at my disposal for a summer and to acknowledge his kind assistance and many suggestions while carrying on the work.

PHYSICAL LABORATORY,
BRADLEY POLYTECHNIC INSTITUTE,
PEORIA, ILL.

THE RELATION BETWEEN "POTENTIAL TEMPERATURE" AND "ENTROPY."[1]

By L. A. Bauer.

IN 1888 the late Professor von Helmholtz incidentally introduced the term "waermegehalt" in connection with his investigations,[2] "On Atmospheric Motions." According to him the "waermegehalt" or the actual heat contained in a given mass of air is to be measured by the absolute temperature which the mass would assume if it were brought adiabatically to the normal or standard pressure. It remained for the late Professor von Bezold, however, to perceive the full significance of this term and to reveal its important bearing in the discussion of meteorological phenomena.

As the quantity really involved in this new term is not a quantity of heat, von Bezold suggested that the term be replaced by the evidently more appropriate one of "potential temperature."[3] This met with von Helmholtz's approval.

With the aid of this happy idea of "potential temperature" von Bezold was enabled to draw in a simple and beautiful manner a number of important conclusions governing thermodynamic phenomena taking place in the atmosphere. Thus, for example, he found that:

"Strict adiabatic changes of state in the atmosphere leave the potential temperature unchanged, whereas pseudo-adiabatic ones invariably increase the same, the increase being in proportion to the amount of aqueous evaporation."

Von Bezold called attention to the fact that this law bears a strik-

[1] Presented before the Philosophical Society of Washington, March 16, 1907.

[2] Sitzungsberichte Berliner Akademie, 1888, V. XLVI., p. 652, "Ueber atmospherische Bewegungen," see translation in Abbe's Mechanics of the Earth's Atmosphere, Washington, 1891, p. 83. The symbol θ is used to denote the "Waermegehalt."

[3] Sitzb. Berliner Akad., 1888, V. XLVI., p. 1189, "Zur Thermodynamik der Atmosphaere"; also in von Bezold's "Gesammelte Abhandlungen," Vieweg und Sohn, Braunschweig, 1906, p. 128. A translation will be found in Abbe's Mechanics, etc., p. 243.

ing resemblance to the well-known theorem of Clausius, now commonly known as the second law of thermodynamics, viz.: "that the entropy strives towards a maximum;" but, he says, "it is not identical with it."

The purpose of this paper is to examine into the precise relationship between the two functions "potential temperature" and "entropy" and to see whether any use could be made advantageously of the former in the treatment of certain thermodynamic problems as well as to ascertain wherein the potential temperature law fails to give full expression of the second law of thermodynamics. To my knowledge no application has as yet been made of the new term in treatises on thermodynamics. The substance of this paper was communicated to the American Association for the Advancement of Science at the Springfield meeting in 1895, but publication pending opportunity for further elaboration was deferred.

The "potential temperature" of a body is defined as the absolute temperature assumed when the body is brought adiabatically to standard pressure.

Defining the thermodynamic state per *unit of mass* of a body by the three variables, T, the absolute temperature, v, the volume per unit of mass, p, the pressure supposed uniform, the following characteristic equation subsists between them: $T = f(v, p)$.

If the body be brought now adiabatically to standard pressure p_0, then the temperature assumed at the end of the process is the so-called *potential temperature* as above defined and is designated by the symbol θ. Hence,

$$\theta = f(v, p_0). \tag{1}$$

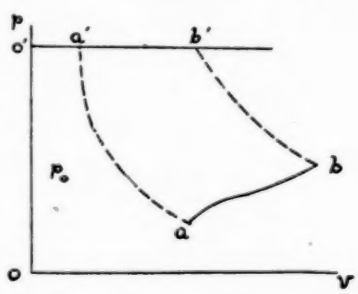
For a perfect gas, since $kT = pv$, k being a constant for any particular gas,

$$\theta = \frac{p_0}{k} \cdot v = k_0 \cdot v, \tag{2}$$

or the potential temperature for any particular gas is directly proportional to the volume and, hence, as von Bezold showed, the potential temperature readily admits of a graphical representation on the usual pv diagram, being simply proportional to the v abscissæ of points of intersection of the line of standard pressure, $p = p_0$, with the adiabats.

Hence, were it possible to express the entropy function for perfect gases directly in terms of potential temperature, we should likewise have for certain cases an easy graphical representation of the entropy function.

In the pv diagram opposite let aa' and bb' represent portions of two adiabats, and $o'a'b'$ be the line of standard pressure $p = p_0$.



Suppose the initial thermodynamic state of the body experimented upon be represented by the point a and some process ab be carried out. According to definition, the potential temperature, θ_a, in the state a will be the temperature at the point along the adiabat aa' where it is intersected by the line of standard pressure. But according to equation (2) the temperature at, this point, a', is proportional to the volume, *i. e.*, to $o'a'$. Similarly the potential temperature in the state b will be proportional to the abscissa $o'b'$. Hence if measured on the same scale, $o'a'$ and $o'b'$ will represent directly for the same substance the respective potential temperatures. It is thus easy to represent graphically at any stage of the process ab the corresponding potential temperature.

If it is desired to determine the numerical value of the potential temperature, this can be done with the aid of the equation of the adiabat thus:

$$\theta_a = \theta_{a'} = T_a \left(\frac{v_a}{v_{a'}}\right)^{\epsilon-1} = T_a \left(\frac{p_0}{p_a}\right)^{\frac{\epsilon-1}{\epsilon}},$$

or

$$\theta_a = \left(\frac{p_0 v_a}{k}\right)^{\frac{\epsilon-1}{\epsilon}} T_a^{\frac{1}{\epsilon}} = k' v_a^{\frac{\epsilon-1}{\epsilon}} T_a^{\frac{1}{\epsilon}}. \qquad (3)$$

$$[\epsilon = 1.41].$$

For a perfect gas, the entropy, s, *per, unit of mass* may be expressed by the following equation:[1]

$$s = \int -\frac{dh}{T} = c_v \log T + k \log v + \text{const.}, \qquad (4)$$

[1] See, *e. g.*, Planck's Thermodynamics.

c_p and c_v are, respectively, the specific heats at constant pressure and at constant volume; k is a constant for any particular gas. Utilizing equation (3) and remembering that

$$\varepsilon = \frac{c_p}{c_v} \quad \text{and} \quad k = (c_p - c_v)$$

we get

$$s = c_p \log \theta + (\varepsilon - 1) \log \frac{k}{p_0} + \text{const.},$$

or

$$s = c_p \log \theta + \text{const.} \tag{5}$$

This gives us the relation sought between potential temperature and entropy. Since c_p is invariably a positive quantity, it follows at once that for any process the potential temperature varies in precisely the same direction as the entropy. If the entropy is increased, as it invariably is for irreversible processes in accordance with the second law of thermodynamics, then is the potential temperature likewise increased. When the entropy remains constant, as for reversible processes, *e. g.*, a strict adiabatic process, then the potential temperature likewise remains constant. In other words as far as perfect gases are concerned it is possible to express the entropy function in its simplest form by means of a quantity — the potential temperature — not only readily interpretable but also easy of direct graphical representation.

Owing to the intimate relationship between entropy and potential temperature the term "entropic temperature" might appear as being possibly a more suggestive one for von Helmholtz's "waermegehalt" than that of "potential temperature," but it may hardly seem advisable now since von Bezold's extensive use of the latter term to recommend a change.

Cyclical Process. — By turning back to the diagram, it will be seen that the change in potential temperature in going from a to b is precisely the same as from a' to b', *i. e.*, the same as for a simple expansion process under constant pressure. Hence, in carrying out the cyclical process $abb'a'a$, it will readily be seen that the sum total of the potential temperature changes is zero, just as in the case of the sum total of the entropy changes.

We have in general:

$$s_b - s_a = c_p(\log \theta_b - \log \theta_a) = c_p(\log \theta_{b'} - \log \theta_{a'}), \qquad (6)$$

or the entropy change in passing from a to b by any process whatsoever — reversible or irreversible — can be measured ideally by the temperature changes incurred in allowing the body to expand under standard pressure between the initial and final adiabats.

For other Substances. — If the substance acted upon be not a perfect gas we have:

$$\int_a^b ds = s_b - s_a = \int_{a'}^{b'} -\frac{dh}{T} = \int_{a'}^{b'} c_p \frac{d\theta}{\theta} = \int_a^b c_p \frac{d\theta}{\theta}. \qquad (7)$$

Here c_p is not a constant as in the case of a perfect gas, but varies with temperature and may even be discontinuous, hence it is impossible, in general, to carry out the integration of the right-hand member. This we know, however, that c_p is invariably positive, *i. e.*, heat must always be *supplied* to a substance to raise its temperature under a constant pressure. Since

$$ds = c_p \frac{d\theta}{\theta}, \qquad (8)$$

it follows that the sign of ds is the same as that of $d\theta$, so that whenever the entropy increases, the potential temperature does likewise. This, while true for cases treated, is not so, in general, as previously explained.

In the foregoing paragraphs the law of potential temperature has been deduced from that of entropy, however, an independent deduction can readily be made if desired.

For example, we may build up the law of potential temperature in precisely the same manner as in the case of the entropy law by taking typical examples of natural processes and showing that nature unaided invariably tends to increase the potential temperature.

Thus take the well-known case of the sudden expansion of a perfect gas without the performance of external work. It is very easy to show on the pv diagram, since the adiabat is a steeper curve than the isotherm, that the potential temperature in the final stage is greater than in the initial stage.

So again with the case of heat conduction. Suppose we have the same mass of the same perfect gas enclosed in each of two vessels a and b of the same size and enclosed in a non-conducting vessel. The temperature of a is greater than b. Connect now a and b thermally whereupon in accordance with nature's law heat will flow from the hotter body to the colder until the two are of the same temperature. It will be found that here again the potential temperature of the entire system at the end of the process is greater than at the beginning. This may be proven most readily thus: For a perfect gas we have from (3), when the volume remains constant:

$$\theta = k' T^{1/\varepsilon},$$

hence

$$d\theta = \frac{k'}{\varepsilon} \cdot \frac{1}{T^{\mu}} dT,$$

where $\mu = 1 - 1/\varepsilon =$ positive quantity, since $1/\varepsilon < 1$. Consequently, *the change in potential temperature for a given change in absolute temperature, the volume remaining constant, decreases with absolute temperature.* Hence, although the two bodies, a and b, under the conditions imposed, change in absolute temperature by the same amount, the first losing, the second gaining, because of the law just stated, the potential temperature of the colder body, b, suffers a greater increase that the decrease in potential temperature experienced by the warmer body, a, which was to be proven.

So also for imperfect gases the law of increase of potential temperature for natural processes can be established independently of the entropy principle. It is merely necessary to show that in general the adiabat is steeper than the isotherm or that the change in potential temperature varies inversely with the absolute temperature, when the volume remains constant.

Thus far it has appeared as though the potential temperature law might suffice equally as well as the entropy law. However, in all thermodynamic problems where the element of mass enters, the former law necessarily fails to give as complete a representation of the second law of thermodynamics as the entropy law. The entropy function is not alone a function of pressure and volume but also of mass whereas the potential temperature is independent of

the latter. Equation (8) shows likewise that the substitution of the obviously more convenient function — potential temperature — for entropy cannot be made in general. There are doubtless, however, a number of thermodynamic problems as was shown by von Bezold, as also in this paper, where the application of the potential temperature law may be found convenient. The main purpose of this paper, as above stated, has been to show the precise relationship between the two functions.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-NINTH MEETING.

THE annual meeting of the Physical Society was held in the Ryerson Physical Laboratory of the University of Chicago during the week beginning Monday, December 30, 1907. The meeting was a joint meeting with Section B of the American Association for the Advancement of Science. Sessions for the presentation of papers were held on December 30, 31, 1907, and January 1, 2, 1908.

The annual business meeting of the Society was held on Wednesday, January 1, 1908.

Tellers being duly appointed the ballots for the annual election were counted and the following gentlemen were declared elected as officers of the Society for the year 1908:

President. — E. L. Nichols.

Vice-President. — Henry Crew.

Secretary. — Ernest Merritt.

Treasurer. — J. S. Ames.

Members of the Council. — W. C. Sabine and S. W. Stratton.

The Council brought before the meeting a request from the College Entrance Examination Board that the Physical Society coöperate with it in the formation of a Commission to consider the revision of the definition of the Board's present entrance requirement in Physics.

After discussion it was moved, and carried by a large majority, that the invitation be declined on the ground that the teaching of Physics and all pedagogical matters lie outside the province of the American Physical Society.

The following papers were presented:

1. Note on Spark Potentials. R. F. EARHART.

2. The Discharge of Electricity from Pointed Conductors. JOHN ZELENY.

3. The Influence of Humidity upon the Electrical Discharge from Points in Air. JOHN ZELENY.

4. A Null Reading Instrument for the Measurement of Ionization. [With demonstration.] S. J. ALLEN.

5. Radioactivity of a Smoke-laden Atmosphere. S. J. ALLEN.

6. On the Value of the Charges Carried by the Negative Ion of Ionized Gases. R. A. MILLIKAN and L. BEGEMAN.

7. The Distribution of Ionizing Energy about an X-ray Tube in Action. W. R. HAM.

8. The Velocity of the Negative Ions Produced by the Ultra-violet Rays. ALOIS F. KOVÁRIK.

9. The Variation of Apparent Capacity of a Condenser with the Time of Discharge and the Variation of the Capacity with Frequency in Alternating Current Measurements. BRUCE V. HILL.

10. The Capacity of Paper Condensers and Telephone Cables. ANTHONY ZELENY and A. P. ANDREWS.

11. An Examination of Certain Alternating Current Circuits, Including those Containing Distributed Capacity. CARL KINSLEY.

12. A Comparison of the Formulas of Helmholtz and Nernst for the Electromotive Force of Concentration Cells. HENRY S. CARHART.

13. Determination of the Fusion Points of Sodium Nitrate and Potassium Nitrate. FLOYD R. WATSON.

14. The Stability of Cadmium Cells. HENRY S. CARHART.

15. On the Separation of Echelon Spectra by Gratings. A. A. MICHELSON.

16. Upon the Magnetic Separation of the Spectral Lines of Barium, Yttrium, Zirconium and Osmium. B. E. MOORE.

17. Heat of Evaporation of Water. A. W. SMITH.

18. A Satisfactory Form of High Resistance. G. W. STEWART.

19. A New Apparatus for Measuring Electrolytic Resistance. ARTHUR W. SMITH.

20. The Resistance Temperature Coefficient and the Coefficient of Expansion of Carbon. G. W. STEWART.

21. The Temperature Coefficient of the Moving Coil Galvanometer. A. ZELENY and O. HOVDA.

22. The Use of Complex Quantities in Alternating Currents. G. W. PATTERSON.

23. Physical Research at a Mountain Observatory. George E. HALE.

24. Some Cases of Excessive Damping of Torsional Vibrations. K. E. GUTHE.

25. The Effect of Tension on Thermal and Electrical Conductivity. N. F. SMITH.

26. The Electric Double Refraction of Carbon Bisulphide. CHARLES F. HAGENOW.

27. Phonographic Record of the Doppler Effect. CHAS. T. KNIPP.

28. An Investigation of the Optical Properties of Films of Magnetic Metals. C. A. SKINNER and A. Q. TOOL.

29. The Distribution of Energy in the Spectrum of the Tungsten Filament. (Read by title.) R. E. NYSWANDER.

30. The Infra-red Absorption of Certain Biaxial Crystals for the Three Principal Directions of Vibration. R. E. NYSWANDER.

31. Ionization of Gases at High Pressures. HENRY A. ERIKSON.

32. The Susceptibility of Copper and Tin and their Alloys. O. C. CLIFFORD.

33. The Magnetic Properties of Antimony. ARTHUR L. FOLEY.

34. A Galvanometer Scale for the Direct Reading of Temperatures with Thermo-electric Couples. ANTHONY ZELENY.

35. The Heat of Dilution of Aqueous Salt Solutions. F. L. BISHOP.

36. How does a Violinist Control the Loudness of his Tone? HARVEY N. DAVIS.

37. A Repetition of the Wheaton Experiment of 1834. FRANCIS E. NIPHER.

38. Some Curious High Temperature Phenomena. C. E. MENDENHALL.

39. On the Variations in the Penetrating Radiation from the Earth. C. S. WRIGHT.

40. On the Radioactivity of Potassium Salts. J. C. MCLENNAN.

41. On the Absorption of Short Electric Waves by Air at Different Pressures. J. E. IVES and R. E. C. GOWDY.

42. A Hydrogen Peroxide Cell. (Read by title.) H. T. BARNES and G. W. SHEARER.

43. The Spectrum of Calcium. (Read by title.) JAMES P. BARNES.

44. Selective Reflection as a Function of the Atomic Weight of the Base. (Read by title.) W. W. COBLENTZ.

45. A Wave Machine Showing Damped or Undamped Compound Waves. (Read by title.) ALBERT B. PORTER.

46. Notes on Harmonic Analysis. (Read by title.) ALBERT B. PORTER.

47. A Mechanical Effect Accompanying Magnetization. (Read by title.) O. W. RICHARDSON.

48. A Relation of Mass to Energy. (Read by title.) DANIEL F. COMSTOCK.

49. Absorption Spectra of Roentgen Rays measured by a Radiometer. (Read by title.) J. M. ADAMS.

50. The Use of the Bunsen Ice Calorimeter for Accurate Heat Measurements. (Read by title.) H. T. BARNES and F. H. DAY.

The meeting adjourned at noon on Thursday, January 2, 1908.

ERNEST MERRITT,
Secretary.

An Investigation of the Electric Displacement and Intensities Produced in Insulators by Their Motion in a Magnetic Field, and its Bearing on the Question of the Relative Motion of Ether and Matter.[1]

By S. J. Barnett.

If a particle with electric charge q moves with velocity v in a magnetic field whose induction is B, it is acted upon by a force

$$F = VvB. \qquad (1)$$

Hence in a portion of matter moving in a magnetic field there is, on the theory of Lorentz, according to which matter is built up of electrified constituents and the ether is at rest, an intrinsic electric intensity

$$e = F/q = VvB \qquad (2)$$

acting on the matter only, but not on the permeating ether. The resulting displacement of the particles of matter gives rise to an electric field intensity E acting on both matter and ether, the actual electric displacement at any point depending on both intensities and on the dielectric constant of the medium. If the ether moves with the matter, it also is acted upon by the intrinsic intensity VvB, and the resulting displacement will be different. The intensities, displacements, e.m.f.'s, and charges can be calculated without difficulty in certain simple cases suitable for experimental discrimination between the two theories.

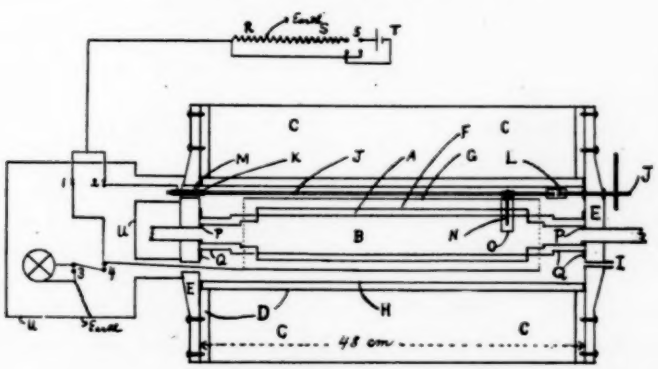


Fig. 1.

In my experiments the insulator under investigation has the form of a hollow circular cylinder A, Fig. 1, fitted closely on a coaxial rotor B, of bronze. This rotor revolves centrally and symmetrically within a large

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 19, 1907.

cylindrical coil C of copper wire wound on a brass bobbin DD. The magnetic field is produced by a current in this coil. The bearings EE in which the rotor B moves are of lumen screwed to the flanges forming the ends of the bobbin DD. The cylinder A is covered with a thin conducting coat F. A little longer than A, and surrounding it coaxially, is a uniform brass tube G. Surrounding this are the coaxial brass tubes H and D, the latter a part of the bobbin, and both together forming, with the brass rings soldered between them at the ends, a jacket for water or air. The tube G is insulated from H by small blocks of amberoid. Between these tubes is a brass rod JJ, capable of being rotated in the brass bearings K and K near its ends. The rod is cut near its right end and the two parts are separated by a block of amberoid L. At the left end the bearing K is insulated by means of a surrounding amberoid block M. Screwed to the insulated part of the rod JJ is a brass wire N, by which it may be brought into contact with the metal coat F of A without touching the tube G. For this purpose a small slit O is cut in G. Small ebonite rings PP make the electrical contacts between the rotor and the bearings always nearly the same. Brass tubes QQ of very nearly the same diameter near A as that of the part of the rotor within A, and coaxial with A, extend from the bearings almost into contact with B, and form electric screens. Except as shown in the figure, the space within C is practically metal-enclosed. A slow stream of dry dust-free air enters through the tube I. A potentiometer RS and battery T, with commutator 5, produce the voltage (along R) used for standardization purposes. Amberoid keys 1, 2, 3, 4, of special design, connect G and J with the battery and an electrometer, all connections being made within the brass case U, which is earthed. The rotor is driven at various speeds by an electric motor.

The observations, aside from those involved in preliminary experiments and in the determination of certain constants, consist of two parts, (1) calibration, and (2) experiment proper. In (1), keys 1, 2, 3 are initially closed, N is down, or in contact with F, and 4 and 5 are open. Then, in succession, 5 is closed, N is raised, 5 is opened, 1 is opened, 4 is closed, 3 is opened, N is lowered, and the electrometer scale reading is taken. The process is repeated with 5 reversed. The double deflection d_0 corresponding to the voltage V_0 along R is determined. In (2), keys 1 and 5 are initially open, 2, 3, 4 closed, N down, the rotor at rest, the current in the coil zero. Then, in succession, N is raised, the motor is started, the coil circuit is closed, the current is determined, 3 is opened, the coil circuit is broken, the motor is stopped, N is lowered, and the electrometer scale reading is taken. The process is repeated with the current in the coil reversed. The double deflection d corresponding to the coil current I and the period T of the rotor (recorded

by a chronograph) is thus found. All the operations are so timed as to eliminate as many errors as possible.

If now K denotes the dielectric constant of the medium under investigation, φ the mean magnetic flux per unit current in the coil across a right section of the hollow cylinder A, φ' the mean flux per unit current in the coil across a right section of the metal cylinder F, and V the mean voltage from the surface of the part of the rotor within A to the earth, it follows from Lorentz's theory as developed for the above experiment that

$$\frac{d}{d_0} V_0 = \left(\varphi \frac{K-1}{K} + \varphi' + V \right) \frac{I}{T} \tag{3}$$

or

$$\frac{T}{I} \frac{d}{d_0} V_0 - (\varphi' + V) = \varphi \frac{K-1}{K} \tag{4}$$

suitable units being used. If the ether moves with the matter, unity must be substituted for $(K-1)/K$.

Two series of experiments have been completed, one with a cylinder of sulphur, the other with a cylinder of rosin. In each case $\frac{d}{d_0} V_0$ was found to be proportional to I/T as required by either (3) or the corresponding equation for the ether-motion theory.

In the case of sulphur the mean value of

$$\frac{T}{I} \frac{d}{d_0} V_0 - (\varphi' + V)$$

was $0.0^4 1077$, while φ and $\varphi \frac{K-1}{K}$ were respectively $0.0^4 1450$ and $0.0^4 1077$, equation (4) being thus confined within a fraction of 1 per cent. This closeness of agreement is to some extent accidental, as the observations differed much more widely among themselves.

In the case of rosin, the mean value of

$$\frac{T}{I} \frac{d}{d_0} V_0 - (\varphi' + V)$$

was $0.0^5 792$, while φ and $\varphi \frac{K-1}{K}$ were respectively $0.0^4 1308$ and $0.0^5 870$, the theory of Lorentz being again confirmed, though not so closely as before.

Further experiments, on different insulators and with improved conditions, are in progress.

In an investigation on this subject begun later than this one, but published in 1904,[1] Dr. H. A. Wilson, of Trinity College, Cambridge, gave,

[1] Phil. Trans. Roy. Soc.

with the assistance of Professor Larmor, formulæ for his experiment which are incomplete and incorrect. The correct formula is

$$q_0 \frac{d}{d_0} = [(K-1)S_0\varphi + S(\varphi' + V + V') + S'V'] \frac{I}{T} \qquad (5)$$

proper units being used. Here φ, φ', V, I, T, and K have the same meanings as in (3) and (4); S_0 is the capacity the ebonite cylinder would have if ebonite were replaced by ether and the electric field were confined to the region between the coats, and if the lines of intensity were all straight; S is the actual capacity of the ebonite condenser so far as this depends on the tubes of displacement stretching between the outer coat and the inner cylinder; S' is the capacity of the tubes stretching between the outer coat and the case, but *does not include* the capacity S'' of the electrometer, brush, and wires, which *do not revolve*; V'' is the mean voltage from the insulated electrometer quadrant and brush to the outer surface of the outer coat of the ebonite; d_0 is the electrometer deflection when the outer coat and connections have the charge q_0; and d is the electrometer deflection produced when the ebonite revolves in the magnetic field. Instead of S_0, Wilson has what he considered the actual capacity the condenser would have with air substituted for ebonite, so far as tubes of displacement stretching between the outer coat and the inner one are concerned; for S', he has $S + S''$, neither of which was determined separately. Hence it is impossible to say what is the discrepancy between his results and those called for by the theory of Lorentz. Attention has already been called[1] to another error in Wilson's theory, which, however, did not affect his experimental work or calculations.

The troublesome terms S' and V'' in the above formula, and with them what was perhaps the greatest experimental difficulty with which Wilson met, can both be eliminated by surrounding the rotating cylinder and brush with a second cylinder also connected with the electrometer or brush by a wire at rest.

ON THE EMISSIVITY OF MOLTEN IRON AND COPPER.[2]

BY CHARLES B. THWING.

NUMEROUS attempts made by the writer and others, to measure the temperature of molten iron with the Féry radiation pyrometer led invariably to results which were obviously much too low. The pyrometers employed were, in some cases, furnished for the express purpose of measuring the temperature of molten iron yet the reading obtained by

[1] Roy. Soc. Proceedings, 1905.

[2] Read before the American Physical Society, October 19, 1907.

pointing the telescope at the flowing iron was considerably less than that from the same iron as it solidified in a ladle. Similar experiments tried with the writer's radiation pyrometer, which, like that of Féry, makes use of the total radiation from the surface of the metal, led to the obvious conclusion that the emissivity of clean molten iron is much less than that of a black body, which solid iron approaches quite closely.

As no data were available a series of experiments was undertaken to determine, at least roughly, the constant of radiation for iron and copper since the importance of a knowledge of the temperature of these metals in various industrial operations is coming to be recognized by metallurgists as of considerable importance, and the principle of total radiation offers an extremely convenient means of making such measurements.

Apparatus. — The radiation pyrometer employed consists of a receiving tube and a portable galvanometer. The receiving tube is of light steel oxidized to blackness on its inner surface and is 90 cm. long and 25 mm. in diameter. At the front or receiving end, a diaphragm determines the angular aperture in conjunction with a conical mirror placed about 70 cm. distant near the other end of the tube which is held in the hand when the tube is pointed at the surface whose temperature is to be measured. The radiations are received near the apex of the mirror upon a thin couple of iron-constantan which reaches a state of thermal equilibrium in about 2 seconds after exposure to the radiations. Since all radiations reaching the mirror are transmitted by multiple reflection to the surface of the couple regardless of their direction the instrument is in focus for all distances. The angular aperture being constant the indications are independent of the distance of the object so long as the surface is larger than is required to fill the angle.

The galvanometer is of the pivoted type and therefore does not require leveling, thus making rapid work possible in situations where the time required for setting up and focusing a telescope and leveling the galvanometer would be a decided hindrance. The instrument is compensated for temperature variations in the resistance of the moving coil by an automatic variation of the magnetic reluctance. This arrangement makes unnecessary the introduction of a dead resistance for swamping the variations due to temperature and permits good control of the needle by the control spring with a fairly high sensibility. Three millivolts is sufficient to produce a full scale deflection of 60 degrees. The scale is calibrated by the Stefan-Boltzmann law, $d = K(T^4 - T_0^4)$.

Direct measurement of the temperature of the iron was made by means of two Le Chatelier pyrometers by Keiser & Schmidt. The couples were enclosed in quartz tubes and, in some cases, further protected by iron or graphite tubes. The short life of the couples precluded the taking of a large number of observations by their means.

Method of Observation. — At the iron foundry the iron was drawn continuously from the cupola into a large mixing ladle whence it flowed under a dam into the pouring ladles. The receiving tube was pointed alternately at the stream flowing into and out of the mixing ladle while the Le Chatelier couple was immersed in the ladle, the temperature measured by the couple being considered the same as the average temperature of the two streams. The fall of temperature in the ladle was about 40 degrees.

At the Bessemer plant the Le Chatelier couple was inserted in the fifteen-ton pouring ladle and the radiation measured from the stream as it issued from the botton of the ladle. The stream was here certainly free from all slag and oxide. A similar condition was quite fully realized at the iron foundry by pointing at the lower or back side of the stream.

Results. — For cast iron at 1,300° to 1,400° C. the intensity of total radiation from the molten metal was found to be 0.29, and for mild steel at 1,600° to 1,650° C., 0.28, that of the radiation from solid metal at the same temperatures.

Observations made upon open-hearth furnaces within the furnace, where black body conditions obtain, and at the stream as it issues from the furnace, indicate that the value found holds for temperatures up to 1,800°.

A smaller number of observations made upon copper gave a value for the emissivity of that metal in the molten state of but half that of iron or 0.14 that of a black body. The low emissivity of molten copper has been remarked by workmen, who find that molten copper in the ladle burns the face much less than the same copper when cooling in large ingots where the exposed surface is about the same as in the ladle.

Large numbers of measurements of molten iron give concordant results and point to a constancy of the constant for molten metal sufficient to permit of the use of the same pyrometers as are used for solid metals by the use of a factor or by employing two scales.

HEAT OF EVAPORATION OF WATER.

BY ARTHUR WHITMORE SMITH.

THE heat of evaporation of water is one of the important constants of nature. It has far-reaching practical applications, especially at high temperatures, while at low temperatures it enters into many problems of the physicist, the chemist and the meteorologist. Unfortunately few determinations have been made at ordinary temperatures, and my

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

recent work [1] was undertaken to fill this gap. The method employed was to draw a stream of dry air through water within a calorimeter and determine the amount of water evaporated by again drying the air and weighing the water thus collected. Heat to maintain a constant temperature was supplied by an electric current and the results are expressed in terms of international joules per gram of water evaporated.

The present paper [2] gives the final corrected results expressed in terms of "mean calories" as well as in joules. The true value of the E.M.F. of a Clark cell at 15° C. is much nearer 1.433 volts than the legal and accepted value, 1.434 volts. It is further shown that the most applicable value of J is that determined by Reynolds and Moorby and corroborated by Barnes, viz., 4.1834 joules per mean calorie. Using these factors and the weight of water corrected for the buoyancy of the air gives the following values:

Temperature Centigrade.	Heat of Evaporation. Joules.	Mean Calories.
13.95	2462.5	588.6
21.17	2446.1	584.7
28.06	2430.2	580.9
39.80	2401.0	573.9

Plotting these values on a sheet of accurately engraved cross-section paper, together with all the results of other investigations at both higher and lower temperatures, gives a concordant curve from 0° C. to 100° C. The agreement is especially good for the range 0° C. to 50° C., while the uncertainty at 100° C. is probably not over 0.2 per cent.

From this curve are obtained the following values, which represent our best knowledge of the subject at the present time:

Heat of Evaporation of Water—0° *C to* 100° *C.*

Temperature Centigrade.	Mean Calories.	Temperature Centigrade.	Mean Calories.	Temperature Centigrade.	Mean Calories.
0	596.3	35	576.9	70	556.3
5	593.6	40	574.0	75	553.3
10	590.9	45	571.1	80	550.3
15	588.1	50	568.2	85	547.3
20	585.3	55	565.3	90	544.3
25	582.5	60	562.3	95	541.2
30	579.7	65	559.3	100	538.0

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

[1] PHYSICAL REVIEW, vol. 25, pp. 145–170, 1907.

[2] To be published in the Monthly Weather Review, Oct., 1907.

THE TEMPERATURE COEFFICIENT OF THE MOVING COIL GALVANOMETER.[1]

BY ANTHONY ZELENY AND O. HOVDA.

THE temperature coefficient of a moving coil galvanometer having a cast-iron magnet, was determined in order that the change in the sensibility could be calculated when the instrument is used at different temperatures.

Since the temperature coefficient depends upon the magnet, the suspensions and the coil, and in different relations for different kinds of measurements, the coefficients of these different parts were determined separately. These are combined in their proper relation to determine the temperature coefficients for current, potential and ballistic measurements.

THE CAPACITY OF PAPER CONDENSERS AND TELEPHONE CABLES.[1]

BY ANTHONY ZELENY AND A. P. ANDREWS.

THE free charge[2] capacities of various paper condensers and a telephone cable were compared with their capacities as obtained by the ordinary method where the galvanometer remains connected during the whole period of its throw.

The accuracy with which the free charge can be determined is shown by discharge curves which give the relation between the quantity and the time of discharge. In most cases, the free charge determinations can be made to within one tenth of one per cent., and the capacities as obtained by the ordinary method are shown to be from 2 to 300 per cent. greater than the free charge capacities, the amount of difference depending on the condenser.

Errors are shown to exist in the present methods of determining the specific inductive capacities of dielectrics and in the resistance of dielectrics as obtained by the loss of charge method.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

A MECHANICAL EFFECT ACCOMPANYING MAGNETIZATION.[1]

BY O. W. RICHARDSON.

ON the view that the magnetic properties of bodies are due to the motion of electrons in closed orbits, magnetization is accom-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

[2] A. Zeleny, PHYS. REV., 1906, Vol. 22, p. 65.

panied by the acquirement by the revolving electrons of a resultant moment of momentum about the direction of magnetization. The magnitude of this moment of momentum is calculated, and it is shown that in the general case the moment of momentum per unit volume is proportional to the intensity of magnetization. In the case where all the revolving electrons are of the same sign, the coefficient of proportionality reduces to $2m/e$ where m is the mass and e the charge of an electron. If, as is generally assumed, the revolving electrons in all real bodies are alike as to mass and charge, this coefficient should be the same for all substances. Experiments are being made at Princeton University to detect the existence of this moment of momentum, which should give rise to effects within the reach of experimental measurement.

Notes on Spark Potentials.[1]

By R. F. Earhart.

Point and Plane. — Measurements were made on the P.D. required to cause a discharge between a needlepoint and a plane surface, for very small distances.

Potentials were secured from a bank of storage cells. Distances were measured by means of an interferometer.

Curves are shown representing the relation between distance and potential. One family of curves represents discharge from a positive point for pressures of 75 cm., 37 cm. and 25 cm. In a similar manner results obtained for point negative are shown.

The least potential required for ionization of air under these conditions is 338 volts, a value somewhat less than has been previously determined for plane electrodes.

Potentials less than 338 volts can produce a discharge, but of a different character. Such discharge is probably produced by the projection of corpuscles or metal atoms. The polarity of the point does not influence the discharge for the abnormally small distances. For greater distances discharge occurs more readily from a negative than for a positive point.

Discharge Between Metal Electrodes for Potentials Less than Ionizing Potentials. — Hobbs has shown that discharge produced by potentials less than an ionizing potential depends on the character of the metal electrode. Such discharge can be secured through greater distances if Al electrodes are used than if Pt were employed.

Using electrodes of Pt, Al, and Ag, in the various permutations and plotting P.D. and distance, I have found that discharge is not determined

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

by the character of the negative electrode but rather by the electrode having the lower potential gradient, irrespective of its polarity.

This indicates that the discharge under these conditions is not carried entirely by negative corpuscles.

ON THE ABSORPTION OF SHORT ELECTRIC WAVES BY AIR AT DIFFERENT PRESSURES.[1]

BY JAMES E. IVES AND ROBERT E. CLYDE GOWDY.

IT has been known for some time past that wireless telegraph messages can be sent farther at night than in the day. One of the explanations of this fact which have been advanced, is that the sunlight ionizes the air, and that this ionization causes an absorption of part of the energy of an electric wave.

It was suggested by Professor Louis T. More that this problem could be reduced to a laboratory experiment by sending short electric waves through air enclosed in a glass tube at different pressures and under different conditions of ionization, and determining what absorption of the energy of the wave, if any, occurred under these differing conditions.

This experiment has, in part, been carried out by the authors during the past year.

The electric waves were generated by an oscillator of a modified Righi type, consisting of two small cylinders of platinum, each 25 mm. long and 2.5 mm. in diameter, sealed into glass tubes. The spark between them took place in kerosene oil.

The resonator was of the Klemencic type, consisting of two brass cylinders each 31 mm. long and 2.5 mm. in diameter, connected together by a thermo-electric junction made of fine iron and constantan wires. A Duddell thermo-galvanometer was used to detect the thermo-electric current.

Between the oscillator and the resonator was placed a glass tube, 44.5 cm. long and 10 cm. in diameter, having pieces of plate glass sealed upon its ends. This tube was air-tight, and the air in it could be rarefied by means of a Geryk pump. The oscillator and resonator were each about 2 cm. from an end of the tube. Behind each of them was placed a parabolic cylindrical mirror made of zinc.

The electric waves generated by the oscillator thus travelled through the rarefied air in the glass tube, produced electrical oscillations in the resonator at the other end of it, and caused a deflection of the galva-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

nometer. Any increase in the absorptive power of the air in the tube due to its rarefaction was shown by a decrease in the deflection, and vice versa.

The following results have, thus far, been obtained:

For pressures ranging from atmospheric pressure to about .5 mm. of mercury, there are two pressures which give maxima of absorption and at least one pressure which gives a minimum of absorption. One of the pressures which give maxima of absorption is near the zero of pressure, and the other lies between 40 and 60 cm. of mercury. The pressure of minimum absorption lies between 25 and 35 cm. of mercury. At the pressures which give maxima of absorption the absorption is greater than at atmospheric pressure, while at the pressure of minimum absorption the absorption is less than at atmospheric pressure. Near the zero of pressure the absorption decreases rapidly.

The percentage absorption, namely the ratio of the energy absorbed at any pressure to that transmitted at atmospheric pressure, expressed in per cent., is a small quantity, varying between + 7 per cent. and — 7 per cent. for the whole tube. This gives a percentage absorption per centimeter of length of the tube varying between + .15 per cent. and — .15 per cent.

UNIVERSITY OF CINCINNATI,
December 3, 1907.

ON THE CHARGE CARRIED BY THE NEGATIVE ION OF AN IONIZED GAS.[1]

BY R. A. MILLIKAN AND L. BEGEMAN.

THE paper is a discussion of the sources of error in preceding determinations of e, and a description of attempts to eliminate some of these sources of error. In its essentials the method employed was that used by H. A. Wilson. The source of ionization was radium. The potential difference established between plates 5 mm. apart in the cloud chamber ranged from 1,600 to 3,000 volts. The expansion was of such value as to cause the fall in pressure to be between 22 and 24 cm. of mercury, its initial value being about 75 cm. The cloud was timed as it fell between the cross hairs of a short focus micrometer telescope, so set that the distance between these cross hairs corresponded to an actual fall of 2 mm. The degree of accuracy with which results could be duplicated may be judged from the following typical set of observations.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

Field 2950 Volts. Field off. Time of fall.	Distance between Plates 5 mm. Field on. Time of fall.
5.2 sec.	3.8 sec.
4.8 "	3.8 "
4.8 "	3.6 "
5.2 "	4.0 "
5.6 "	4.0 "
5.6 "	4.0 "
4.8 "	3.2 "
5.2 "	4.0 "
5.2 "	4.0 "
5.2 "	3.6 "
5.2 "	3.6 "
5.2 "	3.6 "
Mean 5.17 sec.	3.77 sec.

Value of e, 4.25×10^{-10} E.S. units.

The results of ten different sets of observations made with fields of the indicated strengths were as follows:

Field Strength.	e
1600 volts 10.67 E.S.	3.81×10^{-10}
2100 " 14.00 "	3.89 "
2400 " 16.00 "	4.10 "
2950 " 19.67 "	4.25 "
1600 " 10.67 "	4.34 "
1600 " 10.67 "	3.66 "
2100 " 14.00 "	4.10 "
2250 " 15.00 "	3.94 "
2350 " 15.67 "	4.37 "
2750 " 18.30 "	3.84 "
Mean	4.03×10^{-10}

DETERMINATION OF THE FUSION POINTS OF SODIUM NITRATE AND POTASSIUM NITRATE.[1]

BY FLOYD R. WATSON.

THE object of the investigation is to determine a series of definite melting points of salts from 300° to 1,400° Centigrade that will be helpful in the calibration of thermo-elements and resistance thermometers.

The determination of the fusion points of the nitrates of sodium and potassium has developed a method that is sensitive, and has opened the way for the more difficult problem of determining fusion points of salts that melt at higher temperatures.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

The salts were melted in a hard glass tube which was surrounded first by a small air space, then by a hot bath of mixed salts. The heating was effected by gas flame and electric current. Temperatures were found by means of a copper constantan thermo-element; the E.M.F. of the latter being determined by a potentiometer. Readings of E.M.F. were taken to microvolts by having the bridge wire of the potentiometer ten meters long, and by arranging the bridge resistance to be only a small part of that of the potentiometer circuit. A certificated cadmium cell was used as a standard E.M.F. The thermo-element was calibrated for ice, steam, and boiling naphthalin and sulphur points.

Results of a number of preliminary observations give the temperature of fusion of sodium nitrate as 307.8° Centigrade, and of potassium nitrate as 336°. Apparatus is now being constructed that will allow these results to be verified with a platinum platinum-rhodium thermo-element, and which will also furnish a means of determining fusion points of salts that melt at higher temperatures.

Ionization of Gases at High Pressures.[1]

By Henry A. Erikson.

THIS paper gives the results of an experimental investigation of the ionization produced in gases at high pressures by the γ rays of radium.

The results show that the current obtained with a constant difference of potential between the electrodes becomes a maximum at a certain pressure and that a further increase in the pressure causes a decrease in the current.

The position of the maximum point depends upon the difference of potential. When the potential difference is 18 volts between concentric cylindrical electrodes separated by about 6 mm., the maximum is at a pressure of 70 atmospheres, and the current at 400 atmospheres is 60 per cent. of the maximum. With a difference of potential of 1,000 volts the maximum is at 150 atmospheres, the current at 400 atmospheres being about 78 per cent. of the maximum.

The results also show that some of the ions remain uncombined for some time after the rays have been discontinued. At the end of an interval of 20 seconds the number of ions obtained from air at 200 atmospheres, with a difference of potential of 1,000 volts, is about 8 per cent. of the number obtained at the end of an interval of 0.1 second, and at 400 atmospheres the number is about 13 per cent. for the same intervals.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

The current-pressure curves for carbon dioxid are approximately similar to those for air, up to the pressure at which the gas liquefies.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
Dec. 7, 1907.

DISTRIBUTION OF IONIZING ENERGY ABOUT X-RAY TUBES.[1]

BY WM. R. HAM.

THE distribution of ionizing energy about X-ray tubes was examined by an electroscope method in order to detetmine whether the uniformity in distribution obtained by previous observers by photographic and fluoroscopic methods would be found to hold.

Working at one and one half meters distance from the center of the tube there was found to be a wide variation in ionizing energy in certain planes. Thus:

1. In the plane determined by the axis of the cathode and the normal to the target there are large variations, the energy along the norml being about one half as great at a point 60° from the normal, where it is a maximum.

2. In the plane at right angles to the preceding plane and containing the normal to the target there are also variations as shown by a large number of curves that cannot be inserted here.

THE EFFECT OF TENSION ON THERMAL AND ELECTRICAL[1] CONDUCTIVITY.

BY N. F. SMITH.

TWO metal bars called A and B of the same material, each $\frac{5}{16}$ of an inch in diameter and about one meter long are mounted horizontally about 10 cm. apart. One end of each bar is held in a clutch made from a heavy block of copper which is heated and maintained at a constant temperature. By means of thermo-electric couples sliding on the bars a point is determined on B which has the same temperature as a given point on A when the steady state is reached. B is then subjected to a stretching force while the condition of A remains unchanged. When the steady state is again reached the couple on B is shifted till it is again at a point where the temperature is the same as at the given point on A. The stretching force is increased, step by step, up to the maximum which the bar will withstand. It is assumed that the thermal

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

conductivity is proportional to the square of the length to the position of the thermo-electric couple. At each step the electrical resistances of the two bars are compared by a modification of Kelvin's double bridge method.

Observations have been made on bars of several different metals and each shows an *increase* in the thermal conductivity with the stretching force. The maximum increase is about 1.7 per cent. At the same time the electrical conductivity *diminishes*, the variation being about the same as that found by other experimenters. The length of time that the stress is applied has a marked effect upon the thermal conductivity.

It is proposed to extend the investigation to torsional and bending forces.

Some Cases of Excessive Damping of Torsional Vibrations.[1]

By K. E. Guthe.

DECREASE of the logarithmic decrement with the amplitude, frequently observed in torsional vibrations, is usually extremely small. It is considered as closely connected with the elastic after-effect. Wires of platinum-iridium which are practically free from such after-effect have not alone a large logarithmic decrement but show also a decided decrease of decrement as well as of period with decreasing amplitude. This is especially pronounced in a 40 per cent. platinum-iridium wire whose logarithmic decrement decreased from 0.0137 to 0.0025, while the amplitudes decreased from 5.7 to 0.85 degrees. The corresponding change in the period was from 7.350 to 7.175 seconds. The decrease in amplitude is nearly proportional to the square of the amplitude. With different moments of inertia suspended from the wire the values of the decrement remained the same for the same amplitudes.

Similar effects, though less pronounced, were observed with wires containing a smaller percentage of iridium and in drawn wires of other materials. It was attempted to explain the phenomena by the assumption that the disappearance of the elastic after-effect is very rapid.

The increase of the logarithmic decrement upon drawing was explained by Beilby's theory of the effect of mechanical hardening. A carbon filament was shown to have a large decrement; the electrolytic deposition of hydrogen upon palladium increased the logarithmic decrement five-fold. In conclusion it was pointed out that the conditions under which a wire is annealed by heating greatly influence its elastic properties.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

Absorption Spectra of Röntgen Rays, Measured by a Radiomicrometer.[1]

By J. M. Adams.

IT has previously been shown photographically[2] that the Röntgen rays from an ordinary focus tube are heterogeneous, that metals show selective absorption toward the different kinds of rays, and that this selective absorption follows different laws with the various metals. The spectrum used in the present paper was obtained by the same method that was used in making the photographs above mentioned, and narrow slits taken from different parts of the spectrum were examined by the radiomicrometer.[3] It was usually found that the beam proceeding from any one of these slits consisted chiefly of rays of one kind, upon which was superposed a small quantity of rays of other kinds. The latter rays were easily removed from the beam by transmission through a metallic sheet of proper thickness, and the beam thus purified satisfied a test for homogeneity, in that its quality, judged by its penetrating power for various substances, was not changed by further transmission through metallic sheets. A beam of rays direct from an ordinary focus tube, on the contrary, shows a decided change of quality after each transmission.

Absorption spectra for metallic sheets of different materials and thicknesses were obtained by placing the radiomicrometer in various regions of the spectrum, and plotting its deflections, reduced by the interposition of the metallic sheet, as ordinates against the distance from one end of the spectrum as abscissa. The resulting curves in some cases were practically straight lines, indicating by their slope that the rays produced by the swiftest cathode particles had the greatest penetrating power; while in other cases there were well marked maxima and minima of absorption in going along the spectrum.

A Wave Machine Showing Damped or Undamped Compound Waves.[1]

By Albert B. Porter.

THIS machine compounds two harmonic waves either or both of which may be of constant amplitude, may have any desired damping coefficient, or may increase in amplitude, at any desired rate. It

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

[2] J. M. Adams, Phil. Mag. (6), 13, p. 576, 1907.

[3] For a description of the radiomicrometer, see J. M. Adams, Proc. Amer. Acad., 42, p. 673, 1907.

thus serves not only to illustrate the ordinary problems in simple harmonic motion, but also the effects of damping by frictional or other resistance, and the phenomena of resonance. It may, for example, be made to portray the effects of resonance in electric circuits, or the decay of speech-currents in telephone cables. The machine simultaneously draws the two component waves, the compound wave, the two circles (or, in the case of damping or resonance, spirals) of reference, and the Lissajous figure which represents the combination of the two harmonic motions.

The machine offers nine choices of ratio of periods between the two simple waves, and each of these ratios may be thrown slightly "out of tune" for the purpose of showing beats, or the changes in the compound wave and the evolutions of the Lissajous figure as the phase progressively changes. There are three choices of wave-length of the fundamental wave. The amplitude of either wave may be given any value between zero and the maximum permitted by the size of the machine; the phase difference can be varied between 0° and 360°; and either wave may be given any desired positive or negative damping coefficient.

Notes on Harmonic Analysis.[1]

By Albert B. Porter.

THIS paper describes: (1) A geometrical representation of the Fourier coefficients of a periodic function as a series of solids; (2) the essential mechanism of an integrating harmonic analyzer which is based on this representation; (3) a new method of harmonic analysis by use of specially ruled sine-coördinate paper, on which the given function is plotted, and the Fourier coefficients are determined by measurement with an ordinary planimeter, and (4) a modified form of the Yule analyzer.

The Use of the Bunsen Ice Calorimeter for Accurate Heat Measurements.[1]

By H. T. Barnes and Franklin H. Day.

IN applying the Bunsen ice calorimeter for measurements of the heating effect of some of the radioactive changes an effort was made to eliminate the uncertainty which always appears in the want of steadiness of the reading. It is a well-known fault with this type of instrument, that the readings are never steady, but have always to be cor-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

rected for a slow freezing or melting going on inside the instrument. The creep or "gang" may be reduced in several ways: Bunsen, 1871, used air-free water and applied a considerable hydrostatic pressure, and still obtained a constant increase in reading (freezing).

Schuller and Wartha, 1888, used the same apparatus with water not air-free and obtained a continuous decrease in reading (melting). Boys, Mond, Ramsay and Shields found a continuous increase in their instrument and compensated for it by surrounding the bulb with an air jacket, thus balancing the freezing by a continuous melting.

Dieterici used a modified form of the Dewar flask, surrounding the calorimeter with a vacuum jacket and thus considerably reduced the creep.

One of the authors, with Mr. Lucas, previously made an effort to reduce the creep by surrounding the calorimeter with freezing-point mixtures of great purity, such as clean, freshly fallen snow and distilled water, but did not succeed. It occurred to the authors, after trying tap water with and without air, and water from clean blocks of river ice, all without success, that it was better to use distilled water, eliminate so uncertain a quantity as the dissolved air, and add a very small quantity of cane sugar to the water before filling the bulb of the instrument.

After several trials with various strengths, it was found that a solution of cane sugar containing .18 gram to the liter practically did away with the creep when the instrument was immersed in clear, cracked river-ice and tap water. The capillary tube of the instrument had a bore of .0006619 c.c. per millimeter, and the actual change in reading which was obtained was less than 5 mm. in 14 hours, and was constant for over two days. Changing the height of the capillary tube was found to have a small effect on the creep.

The authors strongly recommend to those desiring to use the Bunsen ice calorimeter that the bulb be filled with a solution containing from .15 to .18 gram per liter, and boiled free from air. The solution is so weak that the sugar added cannot be detected by its taste, and the arrangement is the simplest way to reduce an otherwise uncertain and troublesome correction.

A HYDROGEN PEROXIDE CELL.[1]

BY H. T. BARNES AND G. W. SHEARER.

TWO papers have been presented before the American Electrochemical Society by one of the authors in conjunction with H. M. Tory and G. H. Cole in which the results of experiments on the effect of

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.

dissolved gases in water on metal surfaces have been given. In the second paper a cell was described which consisted of electrodes of aluminum and magnesium in a solution of aluminum sulphate, to which some hydrogen peroxide was added. Aluminum metal behaves in a peculiar manner in contact with dissolved air, or oxygen, and becomes electronegative to a similar aluminum electrode in water free from dissolved air. Magnesium does not show this effect: hence a cell with the two metals for electrodes has a comparatively large E.M.F. developed when dissolved air or oxygen is introduced. The effect is considerably increased by adding hydrogen peroxide. Acting on the suggestion of Professor Bancroft, tests were applied to the water in which clean aluminum had stood for a few hours, and a measurable quantity of hydrogen peroxide was detected. This was developed from the action of the dissolved oxygen on the aluminum, probably according to the following reaction, also suggested by Bancroft:

$$2Al + 6H_2O + 6O = Al_2(OH)_6 + 3H_2O_2.$$

The amount of yield of the peroxide was considerably increased in several ways. Without dissolved air no trace of peroxide was observed. The generation of the hydrogen peroxide explains the abnormally high E.M.F. developed between two metals so close together in the electrochemical series.

Phonographic Record of the Doppler Effect.[1]

By Chas. T. Knipp.

In this paper an attempt was made to obtain a phonographic record of the Doppler effect. The phonograph was placed at the side of the track, and distant about thirty feet. The horn was directed toward the moving source of sound. A record was taken of a continuous blast of the locomotive whistle sounded over a distance of about 1,000 feet — 500 feet on either side of the position of the observer. By simple calculation it can be shown that the pitch will be lowered one tone when the train velocity is 44 miles per hour or 64 feet per second. The train in question was moving at a velocity of 57 miles per hour or 84 feet per second. The pitch accordingly should be lowered 9.3/8 tones. The phonographic record when reproduced showed a distinct lowering of the pitch — fully a tone as far as it was possible to judge by the ear.

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RADIOACTIVITY OF A SMOKE-LADEN ATMOSPHERE.[1]

BY S. J. ALLEN.

THIS paper gives an account of a series of observations on the rate of decay of the radioactivity of the air at Cincinnati, during the last eight months. The atmosphere at Cincinnati is very smoky and it was therefore thought interesting to observe what effect the smoke particles might have on the rate of decay.

An endless copper wire running over two insulated wooden pulleys was suspended about 20 feet from the ground, and could be charged to a high potential by means of a large static machine. The length between the pulleys was about 180 feet, thus giving 360 feet of wire for the activity to be deposited on.

The active substance deposited on this wire was removed and tested for its activity in the usual manner. In some of the observations the rate of leak method was used and in others the activity was measured by means of the new null reading instrument devised by the author and described in an accompanying paper.

The active substance was collected on the wire under three different conditions: (1) The wire was charged negative, (2) the wire was charged positive, (3) the wire was uncharged.

The active substance deposited was removed from the wire in two different ways. Firstly, by rubbing over the wire a piece of leather moistened with ammonia. Secondly, by rubbing over the wire a piece of thin linen without any ammonia. In some other experiments a lead wire about 50 feet in length was suspended from the copper wire, and afterwards removed and wound in a flat spiral and tested without removing its activity.

Under these various conditions we have the total activity which is deposited on a wire; the part which adheres lightly and the part which can be dissolved off with the outside layer of metal.

About fifty decay curves in all were obtained, extending in some cases over many hours.

These curves were then compared with one another and as far as there was any similarity collected into groups. These groups were then examined to see if there was any simple exponential rate of decay common to all or to part of them.

The main facts brought out in this investigation may be briefly summarized as follows:

1. When the wire was charged negatively a very large amount of activity could be obtained. When charged positively only a small amount.

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When uncharged the amount obtained was quite considerable, the maximum in this way being as great as 25 per cent. of the maximum obtained when the wire was charged negatively.

2. The decay curves obtained differed widely, both with regard to one another of the same method of collection, and to ones of different methods; the period of decay (time taken to fall to have value) varying from 30 to 80 minutes.

3. Only two simple exponential curves could be obtained which extended over any appreciable length of time. One gave a period of about 38 minutes and the other a period of 30 minutes. About one third of the curves were approximately exponential and had a period from 36 to 40 minutes. There thus seems to be a period of decay of about 38 minutes. The rest of the curves were very irregular and had no common characteristic for any length of time. Some of them decayed rapidly at first and then more slowly, whilst others behaved just the reverse.

4. At least eight or ten of the curves showed a slow rate of leak remaining for many hours. In two or three cases this rate of decay was identified with that of thorium excited, having a period of decay of about 11 hours. The fact was brought out that the thorium excited was not always present, and in very variable quantities, the amount in some cases rising to 30 or 40 per cent. of the total. It was found on the uncharged as well as on the negatively charged wire, though in larger quantities in the latter case, and especially when the wire was charged for a number of hours.

5. Whenever possible the amount of thorium excited present was estimated, and this subtracted from the actual curve, and a new curve free from thorium excited plotted. The majority of these new curves give a period of from 28 to 38 minutes. Two of them were almost exactly exponential with a period of 28 minutes, two gave a period of 38 minutes and were nearly exponential, while two had at first a period of 52 minutes, then changing to one of about 28 minutes.

1. On one occasion the activity of the uncharged wire was removed and the wire then charged negatively for an hour. The two curves obtained were in general characteristics similar, and both showed the presence of thorium excited.

One may I think conclude from these results that there is a simple exponential decay with a period of 28 minutes, another one of 38 minutes, and some evidence of a much slower rate of decay with a period of over 50 minutes. If the period is over 60 minutes one can be certain that thorium excited is present. The period of 28 minutes agrees with that of radium. The results of this paper then show that in general the decay curves of the radioactivity of the atmosphere will be irregular and made up of several rates of leak due to radium-excited activity and in many cases also to thorium excited. The effect of smoke particles is un-

doubtedly the same as that of snow, and rain, as observed by other experiments, though the rate of decay is in general different.

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AN INVESTIGATION OF THE OPTICAL PROPERTIES OF FILMS OF MAGNETIC METALS.[1]

BY C. A. SKINNER AND A. Q. TOOL.

THIS paper deals with the magnetic rotation and ellipticity produced by films of iron, cobalt, and nickel of definite thicknesses together with the refractive indices, reflection and transmission of the same.

It appears that two distinct types of films may be produced by cathode deposit *in vacuo*, one a *metallic* the other a *dark* film. The difference does not arise from the gas in which the films are produced for they are alike, whether hydrogen, nitrogen or helium be used as gas filling.

The optical properties of these different types are quite different, and they also differ from those obtained by electrolytic deposition. Both iron and cobalt in the *metallic* type possess magnetic rotary power four times as large as the electrolytic films, while the *dark* types exhibit a rotary power remarkably smaller than the electrolytic. The ellipticity imparted to the transmitted ray is affected to an equal degree.

Dark films of iron have an absorption region in the blue and in this region the magnetic rotation and ellipticity reverse their directions, as might be predicted from the characteristics exhibited by other substances possessing an absorption region in the visible spectrum. *Dark* films of cobalt show also interesting results in the visible spectrum, which duplicate in a sense the results from the iron.

Only *metallic* films of nickel could be obtained and these exhibited effects almost too small to measure.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 30, 1907, to January 2, 1908.